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MINISTRY OF HEALTH.

Methods of Chemical Analysis

as applied to

Sewage and Sewage Effluents

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Report of Committee Appointed to Consider Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents.

Prefatory Note.

A reasonable measure of uniformity is desirable in the methods to be followed in testing the quality of sewage liquors, before and after their purification, and also in the statement of analytical results. Without this, it is difficult to be assured that the same standards are being applied, or that really comparable results are being obtained. Reasonable uniformity is essential if a common language is to be spoken.

This search for some measure of uniformity is not intended in any way as a brake on initiative, upon which progress in methods depends. It should not, however, be difficult to secure both objects, reasonable uniformity and full initiative.

In order to encourage more uniformity, a conference of professional men interested in this subject was called by the Minister of Health. A list is appended of those who were present. As a result, a Committee was appointed further to consider the subject. The Committee was composed of—

Dr. H. T. Calvert (*Chairman*).	Dr. R. A. Lyster.
Dr. S. W. Wheaton.	Dr. G. McGowan.
Dr. J. A. Glover.	Mr. S. E. Melling.
Mr. W. T. Burgess.	Mr. J. A. Reddie.
Mr. J. H. Garner.	Sir Robert Robertson.
Mr. E. Halliwell.	Mr. F. Scudder.
Sir Alexander Houston.	Mr. H. F. Stephenson.

The Committee have presented a report, which is now published:

The Committee have taken as the ground work of their report Part V. of the Fourth Report of the Royal Commission on Sewage Disposal (" Report to the Commission by Dr. McGowan, Mr. R. B. Floris, A.I.C., and Mr. R. S. Finlow, B.Sc., on Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents " : Cd. 1886— IV, 1904). Account has also been taken of a report of a Committee of the Association of Managers of Sewage Disposal Works relating to this subject.

The present report is principally the work of Dr. McGowan, and it is doubtful whether it would have been possible to produce this document without his invaluable assistance, for which the Minister is indebted to him.

Since the report of the Royal Commission was published, a large amount of new work has been done, both in this and in other

countries, and endeavour has been made in the accompanying report to take advantage of it.

It would take too long to enumerate all the changes that have been made in the old report, but the following may be mentioned :—

(1) For the estimation of free and albuminoid ammonia, the importance of using ammonia-free water, rather than water which requires an ammonia correction, is emphasised.

(2) Additional alternative methods are given for the determination of nitrous, nitric, organic and total nitrogen.

(3) For the " oxygen absorbed " from permanganate test, the strength of the permanganate solution has been altered from N/8 to N/80.

(4) As a " stability " test, Scudder's qualitative method for dissolved oxygen absorption by effluents is given in detail, while mention is also made of the American test with methylene blue. The incubator test is also discussed.

(5) Short sections have been added on the determination of alkalinity and acidity and of hydrogen-ion concentration.

(6) The estimation of solids in suspension is described in greater detail than before.

(7) Besides the Winkler method for the determination of oxygen in solution, as modified by Rideal and Stewart, the Miller method is described, while reference is also made to Mohr's method, as modified by Letts and Blake.

(8) The absorption of dissolved oxygen is discussed at length, special reference being made to the 5 days' test, recommended as a standard test by the Royal Commission.

(9) Following this is a section on the determination of the strength of sewage.

(10) The concluding section is a short discussion on the analysis of sludges.

(11) Some of the appendices of the old Report have been left out, while others have been added, namely, comparative tables, by E. Halliwell and by R. Eaton, respectively, on dissolved oxygen absorption in 5 days at 18·3° C., and in 3 days at 26·7° C.; and a table by Ardern, giving comparative figures for oxygen in solution, as determined by the Winkler and by the Miller methods.

The Minister thinks that the present report will prove of signal service to those who are engaged in testing the purity of water and of effluents, and that it will contribute materially to more uniformity, and will in this way help to reduce the difficulty of the many problems which are involved in this matter.

Ministry of Health,
June, 1929.

Conference on Methods of Chemical Analysis, as Applied to Sewage and Sewage Effluents.

Held at

THE MINISTRY OF HEALTH

on

Wednesday, December 10th, 1924.

In the Chair : Mr. I. G. GIBBON, C.B.E. (Assistant Secretary).

Present :—

Dr. S. W. Wheaton	⎫
Dr. H. T. Calvert	⎬ Ministry of Health.
Mr. W. A. Ross	⎪
Mr. R. J. Simpson	⎭
Dr. E. C. Jee	Ministry of Agriculture and Fisheries.
Mr. R. O'F. Oakley	Department of Scientific and Industrial Research.
Sir Robert Robertson	Government Laboratory.
Dr. J. C. Thresh	Essex County Council.
Dr. R. A. Lyster	Hampshire County Council.
Mr. J. H. Coste	London County Council.
Mr. D. R. Wood	Somerset County Council.
Mr. J. T. Thompson	Leeds Corporation.
Dr. E. Ardern	Manchester Corporation.
Mr. J. Haworth	Sheffield Corporation.
Mr. H. C. Whitehead	Birmingham Tame and Rea District Drainage Board.
Mr. Charles N. Tween	Lea Conservancy Board.
Mr. F. Scudder	Mersey and Irwell Joint Committee.
Mr. E. Halliwell	Ribble Joint Committee.
Mr. H. F. Stephenson	Thames Conservancy and Port of London Authority.
Dr. H. Maclean Wilson	⎫ West Riding Rivers Board.
Mr. J. H. Garner	⎭
Dr. G. McGowan	⎫ Institute of Chemistry.
Mr. S. E. Melling	⎭
Mr. W. T. Burgess	Society of Public Analysts.
Mr. J. Garfield	⎫
Mr. W. D. Scouller	⎬ Sewage Works Managers' Association.
Mr. J. A. Reddie	⎭
Mr. G. Bertram Kershaw	
Dr. A. Bostock Hill	Public Analyst.

Report.

1. The Committee have met on 6 occasions. At the first meeting it was considered desirable that the terms of reference to the Committee should be formulated rather more precisely than had been done at the Conference.

2. The following terms were agreed upon :—
   (1) To consider methods for carrying out tests of sewage and sewage effluents, and how the results should be expressed.
   (2) To consider whether it is desirable to include certain tests in all analyses and, if so, which tests.
   (3) To consider tests appropriate for use at small sewage works.

3. At the second meeting of the Committee the observations of individual members on the terms of reference were considered, and it was left with the chairman to draft a report embodying the views expressed. At the third meeting a draft report was considered, and various amendments were made. At the fourth meeting Mr. Gibbon addressed the members of the Committee, who then proceeded to consider in detail the methods of analysis employed by the Royal Commission on Sewage Disposal, and published in the supplementary volumes to their Fourth and Eighth Reports (Fourth Report, Vol. IV, Part V, Cd. 1886–IV ; 1904 and Eighth Report, Vol. II, Appendix Cd. 6943, 1913). They also considered various amendments to the draft report. At the fifth meeting the Committee agreed upon the following form of report, but deferred presentation of the report until the work of reviewing the publication of the Royal Commission on Sewage Disposal, undertaken by Dr. McGowan, had been completed. At the sixth meeting Dr. McGowan's report was considered, and after some slight amendment was agreed to.

(1) *Methods for carrying out tests for sewage and sewage effluents and methods of expressing results.*

4. The methods of analysis for sewage and sewage effluents which the Committee recommend for adoption are set out in principle in the reports of the Royal Commission on Sewage Disposal, but the Committee considered that these reports should be re-written in the light of work which has been carried out since the date of the reports. Much consideration has been given to the various points upon which analysts differ in their procedure, and a certain amount of agreement has been reached. Dr. McGowan has kindly undertaken, with the assistance of the Committee, to re-edit those parts of the Royal Commission Reports dealing with analytical methods in such a way as to embody the general views of the members of the Committee. This task is now completed, and the methods as agreed upon by the Committee are now published.

5. Considering individual tests in some detail, the Committee recommend that in the test for oxygen absorbed from a solution of acid permanganate the strength of the permanganate solution employed should be $\frac{N}{80}$ (0·394 grams $KMnO_4$ per litre), that the temperature at which the test is carried out should be 26·7° C. (80° F.), and that the reaction between the liquid and the permanganate solution should be allowed to proceed (a) for 3 minutes, and (b) for 4 hours.

6. With regard to the test for the determination of suspended matters, the Committee wish to recommend that, where possible, the Gooch crucible method should be adopted, but they are of opinion that in the case of some liquids for which it is not judged possible to adopt this method, centrifuging could be used. The suspended solids should be dried at 100° to 105°C.

7. With regard to the other tests usually carried out, such as estimations of chlorides and of nitrogen in its unoxidised and oxidised forms, the methods described in the following pages should be followed.

8. With regard to the test which measures the rate of absorption of dissolved oxygen from fully aerated tap water, the Committee recommend that for the present the method adopted by the Royal Commission on Sewage Disposal should be followed.

9. The foregoing tests are those which are usually carried out in making a chemical examination of a sewage or effluent. The tests are not by any means exhaustive, and a trained chemist would be able to apply other tests for particular purposes.

10. It was brought to the attention of the Committee that differences in the results obtained by different analysts sometimes arise owing to the lapse of time between the taking of a sample and the commencement of the analysis. The Committee recommend that samples should, if possible, be examined within 24 hours of being taken, but in all cases the time which has elapsed before the analysis is commenced should be stated in the report.

11. The Committee gave consideration to the question of gauging and sampling, and wish to draw attention to the importance of these two operations, especially in cases where samples of sewage are being taken with a view to designing sewage treatment works. The Committee recognise that samples may be taken for various purposes, and that the method of taking the sample as well as the tests to be applied will depend upon the purpose for which the sample is taken. They do not, therefore, make any specific recommendation on these points, but are of opinion that the methods employed for gauging and sampling should be stated when reporting.

12. Accurate gauging, apart from the engineering side of the question, is of the first importance when average samples of a sewage

have to be taken, in order to determine its strength. By " strength " is meant the measure of the amount of oxygen which a given volume of sewage requires for (practically) complete bio-chemical oxidation. 100,000 parts by weight of sewage of average strength require about 100 parts by weight of oxygen. This question is discussed on page 51 *et seq.*

13. The Committee recommend that the results of analyses should be expressed in parts by weight per hundred thousand parts by volume ; that estimations of ammonia, organic nitrogen, nitrites and nitrates should each be expressed in terms of nitrogen ; and that the results of chloride determinations should be expressed in terms of chlorine.

14. The Committee considered whether the examination should be carried out on the sample containing its suspended matter or whether the sample should be settled or filtered before analysis. If the object of the analysis is to form an opinion upon the suitability of the effluent for discharge into a stream, the Committee agree with the recommendation of the Royal Commission on Sewage Disposal that the analysis should be carried out on the sample with the suspended matter included.

(2) *Tests to be included in all analyses.*

15. The tests to be included in any analysis will be determined by the purpose which the analysis is to serve, but, generally speaking, most analyses should include estimations of suspended matter, free and saline and albuminoid ammonia, oxygen obsorbed from an acid solution of permanganate, chlorides, and in addition, in the case of effluents, estimations of nitrites, nitrates and the Royal Commission test for dissolved oxygen taken up from aerated tap water. Care should be taken in referring to the two tests involving the absorption of oxygen that a clear distinction is drawn between these tests as above referred to, viz. :—

    (*a*) oxygen absorbed from permanganate, and
    (*b*) dissolved oxygen taken up from aerated tap water.

(3) *Tests appropriate for use at small sewage works.*

16. Most of the tests enumerated above require the services of trained chemists or assistants having some chemical manipulative skill, but such persons are not usually available at small sewage works. The Committee consider that of the above tests those which could reasonably be expected to be carried out at small sewage works are the tests for oxygen absorbed from permanganate in 3 minutes and 4 hours. In addition, the incubator tests (p. 30) and the indigo reduction test (p. 31, *et seq.*) will be found of value.

18*th May*, 1929.

METHODS OF CHEMICAL ANALYSIS.

General Recommendations ; Expression of Results of Analysis.

The analysis should be put in hand within 24 hours of drawing the sample ; if the interval of time is longer, this should be stated. The analysis should be made on the sample as a whole, *i.e.*, liquid and solid together, unless there are special reasons to the contrary.

Figures of analysis to be given as parts by weight per 100,000 parts by volume, *i.e.*, grms. per 100,000 c.c.*

For quantities between 100 and 1,000 units, record whole numbers ;

,,   ,,   ,,   10 and 100 ,,   record to one decimal place ;

,,   ,,   ,,   1 and 10 ,,   record to two decimal places ;

,,   ,,   below   1   two or three places ;

Ammonia, Albuminoid and organic nitrogen, nitrite and *nitrate* all to be expressed in terms of nitrogen.

Chlorides to be expressed in terms of chlorine.

Alkalinity and *Acidity* to be given in terms of sulphuric acid (H_2SO_4).

NOTE.—The figure for alkalinity, expressed as carbonate of lime ($CaCO_3$), is practically the same as this, *i.e.*, in the ratio of 100 : 98.

Gases (whether as gas or in solution) to be given as parts by weight per 100,000, and also, if desired, as c.c. per litre.

NOTE.—1 part by weight of oxygen per 100,000 volumes=7 c.c. per litre.

Sludges.—Results to be given as percentages of the dry sludge, excepting alkalinity or acidity, which should be in parts per 100,000.

Bulk quantities of sludges to be given in tons per million gallons of sewage.

Volumes dealt with on filters to be given in gallons per cubic yard of filtering material per day.

Temperatures to be given in degrees Centigrade.

Sampling of Sewages and Effluents, etc.

The importance of good sampling cannot be over-rated, as upon this the whole of the deductions depend which are ultimately drawn

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* Although chemical apparatus is now usually graduated in milli-litres, the expression ml., for c.c., has not yet been universally adopted, and in this volume the term c.c. is retained. 1 ml. = 1·000027 c.c. and the difference is, therefore, practically negligible.

from the figures of analysis. With regard to samples generally, every care should be taken to draw them in such a way as to maintain the true proportion of suspended solid to liquid. All samples, more especially effluents, should be drawn quietly, *i.e.*, without unnecessary aeration. Further, it is often advantageous to note the temperature of a sample when drawn. In most cases a half-Winchester quart bottle makes a sufficiently large sample, though for special purposes more is sometimes required. These bottles are filled either full or with only a small air-bubble left at the top, the stopper being then firmly inserted and tied down with a piece of calico. A rectangular wicker basket 16 to 17 inches long, by $6\frac{1}{2}$ inches broad at the top, by 13 inches high, with two partitions, holds comfortably three such half-Winchesters, $10\frac{1}{2}$ inches high, and allows at the same time plenty of room for paper packing ; it is very rare for one of these bottles to be broken in railway transit.

When hourly samples of sewage, etc., are being taken, to be afterwards mixed in sets of 24 samples each, a wide-necked bottle of about 300 c.c. capacity should be filled *completely* every hour and then set aside in a cool place ; at the end of 24 hours these sub-samples should be mixed for the final sample in proportions corresponding to the rates of flow at the respective hours as determined by a gauge. If circumstances do not permit of gauging, then the sub-samples can be mixed in equal volumes, and subsequent allowance made, as far as possible, when reviewing the figures of analysis, for the different factors which tend to cause the mixed sample to be either stronger or weaker than a true average sample taken according to rates of flow. Such hourly samples should of course be collected in normal weather. Excepting on very warm days there is no great change in a sewage (containing no oxidized nitrogen) or effluent within 24 hours after it is drawn. But if a sample cannot be examined on the day that it arrives at the laboratory, it should if possible be kept in an ice box.

In Appendix 1 are to be found four analyses of the same sample of sewage, which had been sub-sampled with the greatest care into four separate bottles, filled completely. These were kept in the light (so far as can be remembered) at laboratory temperature for one, two, three and seven days. From the figures of analysis it will be seen that the sewage, in the absence of nitrate, underwent only slow change during the first two days.

An earlier experiment on the same lines with a sewage containing much nitrite and nitrate showed a rapid loss of nitrogen during the first day. This decomposition has, however, been well established by the work of Adeney and others.*

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* *Cf.* Gayon and Dupetit, (a) *Comptes Rendus*, Vol. 95, p. 644 (*Journ. Chem. Soc.*, Vol. 44, Abs. p. 679) ; (b) *Station Agronomique de Bordeaux*, 1886 (*Journ. Chem. Soc.*, Vol. 50, Abs. p. 823) ; Munro, *Journ. Chem. Soc.*, Vol. 49, p. 651.

Preliminary Notes on Samples in the Laboratory.

Among the points to be noted, before the actual analysis is made, the following may be mentioned :—

1. *Colour.*—This is of most consequence as regards effluents.

2. *Smell.*—This, too, is of most importance in effluents. An effluent may have more or less of a sewage smell when drawn, and a clean smell when it comes to be analysed, the offensive putrescent matter having been oxidized in the interval by the dissolved oxygen and nitrate present. Still, a sample which smells of sewage when drawn is necessarily unsatisfactory. Generally speaking, an effluent which has no smell or an earthy smell is good ; when the smell becomes partly earthy and partly fishy or wormy, the effluent is not of such high class, though it may probably be still good. Sewages and tank liquors should be tested for sulphuretted hydrogen, *e.g.*, by holding a slightly moistened strip of acetate of lead paper inside the top of the bottle (*cf.* also estimation of free and saline ammonia, page 6).

3. *Reaction.*—This is noted by fragments of red and blue litmus paper (a) *in the cold*, allowing them to remain in a small quantity of the liquid for a short time. If they should then show acidity, (b) the liquid may be boiled in order to see whether the acidity is due to mineral acids or merely to carbonic acid. Domestic sewages and tank liquors and effluents from domestic sewages are almost invariably slightly alkaline, excepting percolation effluents from land, which are sometimes highly charged with carbonic acid. If a sample should be found to be permanently acid to any extent, the acidity should be determined before and after boiling (*cf.* also estimation of free and saline ammonia, p. 6).

4. *Matter in Suspension.*—The appearance and (apparent)* quantity of this should be noted, also its colour, whether it is flocculent, etc. Thus, in a sewage the fineness or coarseness is of great moment ; when necessary this sediment should be examined microscopically. Again, the amount of suspended matter in a tank liquor has a manifest bearing upon the length of life of the filter bed on which the liquor is to be treated. Lastly, the quantity and appearance of these solids in an effluent should be carefully noted. If these solids are reddish-brown and well coagulated, the probabilities are that the liquid of the effluent is well or fairly well purified ; but if they are grey and not well aggregated the reverse is most likely the case.

5. It is also desirable to test an effluent sometimes qualitatively for *Lime*, *Sulphates*, *Ferrous* and *Ferric Iron*, etc., in case it should be in any way abnormal.

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* One is not infrequently at fault in making a mental computation of the *weight* of a given sediment (floating or settled), the state of aggregation varies so much.

Determination of (a) Free and Saline Ammonia ; (b) Albuminoid Ammonia.*

Solutions Required.

(1) *Ammonia-free Distilled Water.*—This is conveniently prepared, among other methods, by distilling ordinary tap water with a little permanganate of potash and sulphuric acid, the water remaining pink and slightly acid throughout the distillation ; this procedure constitutes a check against any traces of " organic " ammonia passing over. The acid permanganate must never be allowed to become so concentrated as to generate chlorine from the chloride in the tap water, otherwise the distilled water may be rendered unfit for general use. The deposit of oxide of manganese which gradually settles in the flask and then begins to cause bumping requires to be dissolved out from time to time.

(2) *Ammonium Chloride.*—The ammonium chloride used should be either re-crystallised in small crystals or re-sublimed from the ordinary " pure " salt. It must leave no weighable residue when a reasonable quantity of it is vaporised at a *moderate* temperature in a platinum crucible, and it must also yield the theoretical amount of ammonia upon distillation with pure dilute potash into acid of known strength.

Since in our analyses the figures for the nitrogen in its various forms in sewages and effluents are all expressed in terms of *Nitrogen*, it saves time when calculating results to make the solutions of the strengths :—

(*a*) 3·821 grms. NH$_4$Cl per litre ;
(*b*) 0·03821 ,,   ,,   ,,   (1 c.c.=0·00001 grm. Nitrogen).

Not more than three-fourths of either solution should ever be used, the residue being discarded. Further, it is a useful precaution always to compare, by nesslerizing, a new dilute solution (*b*) with the residual portion of the solution (*b*) which has just been in use ; the two ought, of course, to agree.

(3) *Nessler Reagent.*—Prepared exactly as described in Wanklyn and Chapman's " Water Analysis," fifth edition, page 33, substantially as follows :

A mixture of 35 grms. of iodide of potassium, 13 grms. of corrosive sublimate and about 800 c.c. water is heated to boiling and stirred up until the salts dissolve. After cooling, a cold saturated solution of corrosive sublimate in water is

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* Wanklyn and Chapman, *Journ. Chem. Soc.* for 1867 and 1868.

then cautiously added until the red periodide of mercury, which is produced as each drop of the solution falls into the liquid, just begins to be permanent. In this manner one obtains the solution of iodide of potassium saturated with periodide of mercury, and it remains to render it sufficiently alkaline and to render it sensitive. This is accomplished by adding 160 grms. of solid caustic potash or 120 grms. of caustic soda to the liquid, which is afterwards diluted with water so that the whole volume of the solution may equal 1 litre. In order to render the Nessler reagent sensitive, it is mixed finally with a little more cold saturated solution of corrosive sublimate and allowed to settle. The settlement of the precipitate takes place more readily in presence of that remaining from a previous preparation.

When properly prepared the Nessler reagent has a slightly yellowish tint. If it is perfectly white it is sure not to be sensitive, and it then requires a further addition of solution of corrosive sublimate to render it so.

Before being employed it should be tested by dropping about 2 c.c. of it into a very weak solution of ammonia (strength about ·04 m.grm. Nitrogen in 50 c.c. of water), and if it be in proper condition it will *at once* strike a yellowish-brown tint with the solution.

The stock of Nessler reagent should be kept in a well-stoppered bottle, from which a little is poured out from time to time into a smaller bottle as it is required for use.

(4) *Sodium Carbonate* (free from Ammonia).—An approximately half normal solution, *i.e.*, 26·5 grm. Na_2CO_3 per litre, is a convenient strength.

(a) Estimation of Free and Saline Ammonia.

For the actual estimation of Free and Saline and of Albuminoid Ammonia it is most convenient (and most economical of space) to use large round-bottomed glass-stoppered flasks of about 2 litres capacity and having the delivery tube high up the neck ; for condensation, a Cribb condenser either of block-tin, tin-lined copper, or glass, or a Liebig glass condenser. If the time required for distillation is fairly constant, and if the temperature of the distillate when nesslerized does not vary appreciably, the choice of a distillation apparatus is a matter for personal convenience.

The distilling flask or retort having been carefully cleaned, it is attached to the condenser by a narrow ring of indiarubber (a few m.m. wide when stretched), the delivery tube of the flask or the end of the retort which delivers into the condenser-tube projecting at least 2·5 c.m. below the rubber band. About 200 c.c. of distilled water are now run in, and at least 50 c.c. of this are distilled over.

Should this final cleansing by distillation be omitted, small, but appreciable, traces of ammonia from the vessels themselves may be (wrongly) included in the first distillate of an actual estimation.

500 c.c. of ammonia-free water and 5 or 6 drops of sodium carbonate solution are now poured into the distilling vessel and the sewage or effluent is added by means of a pipette and a long-stemmed funnel, the neck or tubulus of the flask or retort, if warm, being protected from the cold funnel by encircling the shoulder of the latter with about an inch of rubber tubing, split two or three times parallel to its axis for half its length ; the liquid adhering to the funnel is finally rinsed into the distilling vessel with 50 c.c. of ammonia-free water.

The quantity of the sample taken for analysis should be such as to give a distillate for the free and saline ammonia that will correspond to not more than 15 to 20 c.c. of the dilute ammonium chloride solution. One usually takes the equivalent of 1 or 2 c.c. of a sewage, and from 5 to 20 c.c. or even up to 50 or 100 c.c. of an effluent, according to its quality.* Before a sewage or an effluent can be sampled in this way, the liquid and solid in it must be thoroughly mixed, *e.g.*, by stirring up with a thick piece of bent glass rod tipped with rubber. Even then the sampling of a sewage is not always satisfactory. And since it is next to impossible to pipette out 1 or 2 c.c. so as to represent a fair sample of the sewage, a dilution is first made with, say, 25 c.c. sewage plus 225 c.c. of ammonia-free water (*i.e.*, a dilution of 1 in 10), and then 10 or 20 c.c. of this diluted liquid are taken for the actual distillation. This obviates the error of reading very small volumes of liquid, while it also probably gives a truer sample of the mixed liquid and solid.

Should free acid or sulphides be present in the sample to be analysed, sufficient, but no appreciable excess of, sodium carbonate solution (usually 5 or 6 drops) must be added to prevent sulphuretted hydrogen passing over into the distillate ; but any larger addition is not to be recommended, because of the hydrolysing action of alkali upon the organic matter of a sewage or effluent. (See Appendix 2 for the distillation of sewage with water and with different alkaline solutions.) The glass of the distilling vessel furnishes sufficient alkali to ensure all the free and saline ammonia being driven off in the case of ordinary sewages and effluents. (*Cf.* Appendix 3.) But any free acid which may be met with in sewages containing certain trade effluents must, of course, be neutralised in the first instance.

Distillation is then proceeded with, the first fraction being usually one of 150 c.c., which is cooled if necessary and an aliquot portion of it nesslerized. The actual time of distillation of these 150 c.c., from the commencement of the boiling, is about 15 to 16 minutes. The next fraction is one of 50 c.c., and the whole of this is nesslerized ;

* The amount to be taken is arrived at roughly by a preliminary direct nesslerization of a small quantity of the sewage or effluent, sufficiently diluted.

it is usually either free from ammonia or contains only a trace of the latter. Should, however, more ammonia be found in it than corresponds to, say, 0·4 c.c. of the dilute ammonium chloride solution, a further quantity of 50 c.c. of ammonia-free water must be added to the residue in the distilling vessel, and an equal volume distilled off and nesslerized. But, though this is advisable as a precautionary measure, the last-mentioned distillate is almost invariably found to be ammonia-free. The sum of the amounts of ammonium chloride used in nesslerizing represents the free and saline ammonia in the quantity of sample taken ; but this is expressed in terms of nitrogen as *Ammoniacal Nitrogen.*

Two to 4 c.c. of Nessler, run in from a pipette with a wide orifice, are used in each determination. The temperature of the water when nesslerized is of importance ; it should be about 15°–18°C.

(b) Estimation of "Albuminoid" Ammonia.

Solution Required.

{In addition to those already given for the determination of Free and Saline Ammonia) :—

> *Alkaline Permanganate of Potash.*—This is made, after Wanklyn and Chapman, by dissolving 200 grms. of stick caustic potash (or 150 grms. of caustic soda) and 8 grms. of potassium permanganate in about $1\frac{1}{2}$ litres of distilled water, which is conveniently done in an iron basin. The solution is then gently boiled until it is reduced to a volume of about 800 c.c. ; after cooling, it is siphoned into a litre flask and made up to 1 litre with ammonia-free distilled water.
>
> It is tested by adding 25 c.c. of it to about 250 c.c. of ammonia-free distilled water in a retort, distilling over 50 c.c., and nesslerizing this distillate ; the latter must show no ammonia.

Process.—When the residue from the estimation of free and saline ammonia has cooled considerably, 25 or 50 c.c. of the alkaline permanganate are added to the retort or distilling flask from a pipette, and the distillation is proceeded with, the rate of distillation being the same as with the free ammonia. The fractions collected are usually three—of 100, 50, and 50 c.c. respectively. After mixing the first fraction thoroughly, a suitable quantity of it is nesslerized and the " albuminoid " ammonia in the whole fraction is calculated ; the other two fractions of 50 c.c. are each nesslerized as a whole. The sum of the " albuminoid " ammonias in these fractions is expressed in terms of " *Albuminoid Nitrogen.*"

In actual practice this distillation is seldom carried further than the 200 c.c. indicated above, no matter at what rate the albuminoid ammonia may be coming off when this limit is reached. The esti-

mation is thus only approximate, at least in the case of a sewage or an ordinary effluent. If the distillation were carried further (with the addition of successive quantities of ammonia-free water to the retort), albuminoid ammonia would be obtained for an indefinite period in gradually decreasing amounts in the successive fractions of the distillate.

The remarks made on p. 5 with regard to the figures obtained for free and saline ammonia by distillation in glass vessels of different shape apply here also.

NOTE.—*Possibility of "Albuminoid" Ammonia in Distilled Water.*—Although improbable, it is not impossible that traces of albuminoid ammonia may be found in distilled water at times (*cf. Royal Commission on Sewage Disposal*, 4th Report, Vol. IV, p. 15). It would therefore be a wise precaution occasionally to test the distilled water in use, not merely for free but also for albuminoid ammonia.

Estimation of Free and Saline Ammonia by Direct Nesslerization.

Many attempts have been made to estimate free and saline ammonia in sewages and effluents by direct nesslerization, but such a procedure cannot be recommended for quantitative purposes. It may, however, be found useful for giving an approximate result quickly, or with a view to ascertaining what volume should be used for a quantitative estimation.

Estimation of Nitrite by Meta-Phenylene Diamine.[*]

Solutions Required.

(1) *Potassium Nitrite*, containing about 0·00004 grm. of Nitrous Nitrogen per c.c. The preparation of pure potassium nitrite is troublesome, and the ordinary salt containing some nitrate does equally well. The solution must, however, be standardised, both in the first instance and from time to time afterwards, by means of a solution of potassium permanganate of known strength, the excess of permanganate—above that required to oxidize the nitrite to nitrate—being afterwards determined by standard thiosulphate and potassium iodide in the ordinary way (*cf.* Sutton's *Volumetric Analysis*, 11th edition, p. 303). Dilute solutions of potassium nitrite in distilled water, kept in the dark, are comparatively stable (*cf.* Experiments with ammonium nitrite, Royal Commission on Sewage Disposal, 4th Report, Part V., p. 62).

[*] Griess, *Ann. Chem. u. Pharm.*, Vol. 154, p. 333 (1870); Preusse & Tiemann, *Ber.*, Vol. 11, pp. 624, 627 (1878).

When making a nitrite determination in a sample of effluent, 10 c.c. of the above solution are diluted to 100 c.c. with distilled water ; 1 c.c. of this latter solution therefore contains about 0·000004 grm. Nitrous Nitrogen.

(2) *Sulphuric Acid.*—1 part by volume of strong sulphuric acid (free from nitrite) to 3 volumes of distilled water.

(3) *Meta-Phenylene Diamine.*—1 grm. of this substance is dissolved in 200 c.c. of distilled water acidified with 2 c.c. of concentrated sulphuric acid. If the solution should be brown, it must be decolourised by letting it stand over animal charcoal and then filtering. A charcoal containing no phosphate would probably be better. Such a charcoal can be made by saturating Kieselguhr with a suitable organic liquid, drying, and subjecting the mass to dry distillation. The decolourising power of this charcoal is comparable with that of ordinary bone char. Instead of *m*-phenylene diamine itself, its sulphate or hydrochloride may preferably be used (8 grms. hydrochloride dissolved in 1 litre of distilled water acidified with 10 c.c. pure concentrated hydrochloric acid).

Method.—A preliminary trial is made in a Nessler glass with 25 c.c. of the sewage or effluent (filtered unless the sample happens to be clear), by adding to it 1 c.c. each of the sulphuric acid and the *m*-phenylene-diamine solutions, mixing thoroughly, and allowing to stand for 20 minutes. A comparative experiment is at the same time made with, say, 4 c.c. of the *dilute* potassium nitrite solution, also diluted to 25 c.c. with distilled water. At the end of this time the tints are compared, and such a quantity of the sample is taken for the actual estimation as is calculated to give a tint equal in depth to that produced by, say, 4 c.c. of the dilute standard solution, this being a convenient depth of (yellow) colour to read.

The estimation can be done most quickly if several standards are prepared together. Thus, if after the preliminary trial 20 c.c. of the sample were thought to be the proper amount, four standards might be made containing respectively 3·65, 3·80, 4·05, and 4·30 c.c. of the dilute nitrite solution in 50 c.c. distilled water ; one of these would probably match the tint given by the sample. As the yellow colour becomes darker on standing, it is of course essential that sample and standards should have the *m*-phenylene-diamine added at the same time.

For a reading which is close to, but not exactly the same as, one of the standards the exact value can be obtained fractionally. Thus, if both sample and standard have been diluted to 50 c.c., and it is found that 48·5 c.c. of the 4·05 standard give a depth of tint equal to that of the sample, then $(4·05 \times \frac{48·5}{50} =)$ 3·93 c.c. of the nitrite solution will represent the amount of nitrous nitrogen in the volume

of sample taken. This fractional method can, however, only be applied within limits of about 0·5 c.c. of the nitrite solution ; over wider limits the depth of colour produced is not strictly proportional to the nitrous nitrogen present.

Alternative Method.—Where the amount of nitrite is very small, or when the colour in the effluent interferes, the *Griess-Ilosva* method may be substituted.

Estimation of Nitrite by the Griess -Ilosva Method.*

SOLUTIONS REQUIRED.

Sulphanilic Acid Solution.—Dissolve 8·0 grms. of purest sulphanilic acid in 1 litre of 5 N acetic acid (S.G. 1·041). This is practically a saturated solution.

α-Naphthylamine Acetate Solution.—Dissolve 5·0 grms. of solid α-naphthylamine in 1 litre of 5 N acetic acid. Filter the solution through washed absorbent cotton.

Sodium Nitrite Stock Solution.—Dissolve 1·1 grms. of silver nitrite in nitrite-free water, precipitate the silver with sodium chloride solution, filter and dilute to 1 litre.

Standard Sodium Nitrite Solution.—Dilute 100 c.c. of the stock solution to 1 litre, then dilute 50 c.c. of this solution to 1 litre with sterilized nitrite-free water, add 1 c.c. of chloroform and preserve in a sterilized bottle. 1 c.c.=·0000005 grm. Nitrogen.

Aluminium Hydroxide.—This is prepared as in the test for chlorides (p. 35).

Fuchsine Solution.—1 grm. of basic fuchsine per litre.

PROCEDURE.

Place in a standard Nessler tube 50 c.c. of the sample, decolourised if necessary with nitrite-free aluminium hydroxide, or a smaller amount diluted to 50 c.c. At the same time prepare in Nessler tubes a set of standards, by diluting to 50 c.c. with nitrite-free water various amounts of standard nitrite. The following volumes of standard nitrite are suggested :—0·0, 0·1, 0·2, 0·4, 0·7, 1·0, 1·4, 1·7, 2·0, and 2·5 c.c. (containing ·0000005 grm. N per c.c.). Add 1 c.c. of sulphanilic acid solution to 1 c.c. of the α-naphthylamine acetate solution and, if this mixture remains colourless, add it to the sample and a similar amount to each standard. Mix thoroughly and allow to stand for 10 minutes ; then compare the sample with the standards. Do not allow the sample to stand more than 30 minutes

* Griess, *Berichte* for 1879, Vol. 12, p. 426 ; Ilosva L., *Bull. de la Soc. Chim.* Ser. 3, 2, p. 347 ; Warington, *Journ. Chem. Soc.* for 1881, p. 231.

before making the comparison. If the colour of the sample is deeper than that of the highest standard, repeat the test on a diluted sample.

Permanent standards may be prepared by matching the nitrite standards with dilutions of the fuchsine solution. Fuchsine standards have been found to be sufficiently accurate for waters high in nitrite and for sewage. The standards should be checked once a month and kept out of bright sunlight.

Estimation of Nitric and Nitrous Nitrogen together, by reduction to Ammonia with the Copper-zinc couple (Gladstone-Tribe Method.)*

REAGENTS REQUIRED.

(1) and (2) Standard solutions of *Ammonium Chloride* and *Nessler Reagent* (see p. 4) :—

(3) A 3 per cent. solution of crystallised *Sulphate of Copper* ($CuSO_4+5Aq$).

(4) Pure dry *Sodium Chloride*, prepared as given on page 35.

(5) Solution of *Bicarbonate of Lime*, prepared by saturating lime water with washed carbonic acid gas. Such a solution contains about 0·00304 grm. CaO in 1 c.c.

(6) Pure thin *Zinc foil* (see below). It is an unnecessary expense to have this foil thick. A piece which measures about 10 c.m. by 7 c.m. need not weigh more than 2 to 3 grms.

Method.†—One great point in regard to this method is *not to take more* of the sample for nitrate estimation than will ultimately correspond to about 15 c.c. or so of the standard dilute ammonium chloride. As preliminary and supplementary to this process, it is advantageous to use the approximate method with pyrogallic acid, which is described on page 17. A preliminary trial with pyrogallic acid (which can be carried out in a few minutes) tells one pretty nearly how much nitrate and nitrite have to be dealt with, and thus greatly helps the correct quantitative estimation, this being especially the case with highly nitrated effluents. Unless this plan be adopted, the volume of sample taken for nitrate estimation by the couple has to be more or less guessed at, the consequence being that sometimes too much

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* Gladstone & Tribe, *Proc. Roy. Soc.* Vol. XX (1872), p. 218 ; Thorpe, *Journ. Chem. Soc.*, 1873, p. 541 ; Gladstone & Tribe, *Journ. Chem. Soc.*, 1877, p. 561 ; 1878, p. 139 ; 1883, p. 346 ; M. W. Williams, *Analyst*, Vol. 6, p. 36 (1881).

† NOTE.—Some attempts were made to destroy any nitrite present before estimating nitrate, by boiling down the liquid with 0·5 c.c. sulphuric acid. But even when the volume of the liquid had been reduced in this way from 100 c.c. to 25 c.c., much nitrite remained. It is therefore necessary to determine both together, and then to deduct subsequently the nitrite as determined by meta-phenylene-diamine, p. 8).

is used, and a nitrate value in some cases obtained which is appreciably below the true value.

Another important preliminary is to know the amount of free and saline ammonia in the sample. This has probably been determined in the first instance by distillation, or, at all events, an approximate idea has been obtained by a direct nesslerization.

(a) If the amount of ammoniacal nitrogen is comparatively small, say, not more than 0·2 part per 100,000, or if it is not greater than the nitric nitrogen as determined approximately by pyrogallic acid, then 10 c.c. or less of the sample, filtered* if it contains any appreciable solid, is measured by means of a pipette into a wide-mouthed bottle of about 100 c.c. capacity, fitted with a well-ground stopper, 0·2 grm. of the sodium chloride is added,† and the bottle is then filled up to the shoulder with distilled water.

The copper-zinc couple is prepared by loosely rolling a strip of well-cleaned zinc foil,‡ in the direction of its length (about 10 c.m.) and then leaving it completely immersed in some of the 3 per cent. copper sulphate solution (which is never used more than once) until a firmly adherent coating of copper has been deposited on it ; this usually takes about 20 minutes. The roll is then taken out with a pair of forceps, washed well in a basin through which tap water is made to flow gently, and finally in a stream of distilled water, and placed in the already (nearly) filled estimation bottle, the stopper of which must be firmly inserted and tied down. Experience has taught that *a fresh couple must be prepared for each estimation.* If the zinc of a couple, after being cleaned, is used a second time, the copper then appears to be more loosely deposited on it, with the result that the ammonia dribbles over more slowly when the liquid is distilled.

A similar bottle, filled in precisely the same way, excepting that no couple is added to it, gives the "blank," *i.e.*, the free and saline ammonia in the sample and reagents, and no doubt also a little ammonia resulting from the hydrolysis of the organic matter present.

The two bottles are placed in the incubator at 26·7° C. (80° F.) overnight, and next morning the respective contents, plus 100 c.c. of distilled water used for rinsing out each bottle, are distilled from two similar glass-stoppered distilling flasks of about 500 c.c. capacity each. Both distillates are collected in two separate fractions, the

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* The filtration of samples, whether it be for the determination of nitrite, nitrate, or chlorine, &c., is a point deserving attention. The whole of the filter paper in the funnel should be washed several times with the liquid in question, and these washings be rejected ; otherwise the paper may either give up traces of ammonia to the liquid or absorb some constituents from the liquid, or it may do both.

† The addition of the sodium chloride, to accelerate the action of the couple, is absolutely necessary ; if it be omitted, the figure obtained for nitrate in a well-nitrated effluent will almost certainly be too low.

‡ The actual size of the strip which suits the bottle mentioned is about 10 c.m. (4 in.) by 7 c.m. (2¾ in.) and this strip is rolled into a coil.

first fraction of 100 c.c. being received in a stoppered flask of that size, and the second fraction of 50 c.c. in a Nessler glass. The distillation should of course be at the same rate for both.

After shaking up the first fractions from both distillates, two equal measured amounts from both flasks—say 10 c.c. diluted to 50 c.c. with distilled water—are nesslerized separately. By comparing the depths of tint thus produced, an idea is gained of the amount of ammonium chloride which it would be necessary to add to the " blank " distillate in order to make it give as deep a colour with the Nessler reagent as the " couple " distillate does. This operation is repeated at one and the same time with suitable equal quantities of the two distillates until the exact amount of ammonium chloride is determined, which—calculated for the whole 100 c.c. of distillate—corresponds to the nitric plus nitrous nitrogen originally present in the volume of sample taken.

The second fraction of 50 c.c. from both distillates is usually ammonia-free, but it is advisable to add Nessler reagent to the " couple " 50 c.c. first. Any slight colour can then be compensated for, before nesslerizing the " blank " 50 c.c. (which is itself almost invariably ammonia-free), by adding the requisite amount of ammonium chloride to the latter. The ammonium chloride used for this second fraction must of course be added to that required for the first in calculating the total nitric + nitrous nitrogen present. It only remains to deduct the nitrous nitrogen (determined as on p. 8) from this to get at the nitric nitrogen in the sample.

(b) If, on the other hand, much free and saline ammonia are present, 10 c.c. to 50 c.c. (usually 25 c.c.) of the sewage or effluent, filtered if necessary, are diluted to about 150 c.c. with distilled water, 5 c.c. of the calcium bicarbonate solution are added, and the whole is boiled down to about 20 c.c. in a round-bottomed resistance-glass flask, *in a draught cupboard*. This drives off practically all the free and saline ammonia, the presence of the lime salt ensuring the stability of any nitrite present (*cf. Royal Commission on Sewage Disposal*, Vol. IV, Part V, pp. 19–21 and 66–67). The cooled solution is made up to a given volume—say 100 c.c.—with distilled water, and suitable quantities (usually the equivalent of 10 c.c. of the original) are taken both for the " blank " and for the estimation proper.

This boiling down, when much ammonia relatively is present, is of course necessitated by the circumstance that this ammonia appears both in the " blank " distillate and in the distillate from the estimation itself. Since the amount of ammonia to be nesslerized cannot be increased beyond a given limit, save at the expense of accuracy, a much smaller quantity of the sample would have to be taken if there was no boiling down—a quantity in many cases too small to give the accurate figure for the nitrate present.

Experiments made with pure solutions of potassium nitrate have shown that, in order to secure the best results, the liquid to be actually reduced by the couple should not contain more than about 0·2 part nitric + nitrous nitrogen per 100,000, *i.e.*, the ammonia to be actually obtained should not exceed 0·0002 grm. (nitrogen). Quantities of oxidized nitrogen which are markedly in excess of this amount are not always entirely reduced in 18 to 24 hours at a temperature of 26·7° C. (80° F.). But when the above-mentioned conditions are observed, the process is accurate to within 2 or 3 per cent. either way, this being about the limit of accuracy in nesslerizing a pure solution of ammonia.*

Alternative Reduction Method. Aluminium Mercury Method (Ormandy and Cohen†, as modified by Scudder‡).

REAGENTS REQUIRED.

(1) *Normal sodium carbonate solution.*
(2) *Mercuric chloride solution* :—10 grms. per litre.
(3) *Aluminum foil* :—Pure foil in pieces of 5 by 2·5 c.m. (2 in. by 1 in.), weight from ·5 to ·7 grm.
(4) *Hydrochloric acid* :—25 per cent. of the concentrated acid, ammonia-free.

PROCEDURE.

An appropriate volume of the sample, generally from 10 to 25 c.c., filtered if necessary, is measured into a 250 c.c. conical flask and diluted with distilled water to 100 c.c.; 0·5 c.c. normal sodium carbonate solution is then added and the contents of the flask are evaporated down to about 20 c.c.

The liquid is then transferred to a boiling tube, 15 c.m. by 4 c.m., (6 in. by 1½ in.), and the rinsings of the flask added (using ammonia free water), bringing the volume to 50 c.c. Then 5 c.c. of 25 per cent. hydrochloric acid, free from ammonia, are added.

Next, a piece of aluminium foil, which has been amalgamated over the entire surface by immersion in mercuric chloride solution for several minutes, is put in, the mouth of the tube covered with a small watch glass and the action allowed to proceed for a minimum period of 2 hours. Instead of a watch glass, the tube may be closed by a rubber stopper carrying an S-shaped glass tube of about 5 m.m. external diameter, one end of the tube being flush with the lower side of the stopper, and the other end being widened out to contain a little glass wool, moistened with distilled water. This serves as a trap for any spray which might escape along with the hydrogen.

* Purvis and Courtauld, in a paper entitled "The Limitations of the Copper-Zinc Couple in Estimating Nitrates" (*Proc. Camb. Phil. Soc.*, Vol. XIV, p. 446 (1908)), suggest some doubts as to the accuracy of the method for waters which are highly charged with organic nitrogenous compounds.

† R. Ormandy & J. B. Cohen, *Journ. Chem. Soc.*, Vol. 57, p. 811 (1890).

‡ Scudder, *Interim Report, Royal Commission on Sewage Disposal*, Vol. II, p. 332, par. 5999 (Cd. 686).

After reduction the acid solution is made slightly alkaline by the addition of ammonia-free sodium carbonate solution, and the contents of the tube are poured into a distilling flask, diluted with 250 c.c. of ammonia-free water, distilled and the distillate collected in a 200 c.c. flask. The ammonia in the distillate is then determined by nesslerizing exactly in the same manner as in the free ammonia determination.

Nitrometer Method for the Determination of Nitrate and Nitrite together in Sewage Effluents. (Crum.)*

The details of the nitrometer method as applied to drinking waters are given in several works, including Frankland's *Water Analysis* and Sutton's *Volumetric Analysis*.

PROCEDURE.

A known volume of the sewage effluent (100–250 c.c.) is slightly acidified with dilute sulphuric acid and treated with dilute potassium permanganate (N/80) until a faint pink colour persists, the acidity then being neutralised with dilute soda solution. The solution is evaporated to dryness and the residue is extracted successively with small quantities of hot distilled water, the extraction being assisted by rubbing the residue with a rubber-tipped glass rod. The solution and washings, which should not exceed a total volume of 10 c.c., are filtered through a suitable filter paper of three or four centimetres diameter into a small beaker or glass basin and evaporated nearly to dryness. The concentrated solution is then washed into the cup of a *Lunge* nitrometer with hot distilled water, the total volume of solution and washings not being allowed to exceed three or four c.c., and finally run into the burette of the nitrometer, previously filled with mercury.

A volume of concentrated sulphuric acid equivalent to one and a half times the volume of the water solution is then placed in the beaker or glass dish and poured into the cup and finally into the burette of the nitrometer. After allowing the acid and water solution to mix, any air or traces of carbon dioxide are expelled and the liberation and determination of the nitric oxide made in the usual way, regard being paid to the temperature and pressure. (For details, *cf.* Sutton's *Volumetric Analysis*, 11th Edn., p. 449 *et seq.*) Nitric oxide contains half its volume of nitrogen and from the measured volume obtained the weight of nitrogen may be calculated. It is necessary to deduct the nitrogen equivalent of the nitrite, to obtain the nitrate nitrogen.

Effluents containing 0·2 part of nitrate nitrogen per 100,000 give about one c.c. of gas when 250 c.c. of the effluent are taken for the determination.

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* Crum, *Phil. Mag.* (3), 30, p. 426 (1847); Frankland & Armstrong, *Journ. Chem. Soc.*, 1868, p. 101; Warington, *Journ. Chem. Soc.*, 1879, p. 375.

Estimation of Nitric Nitrogen alone ; the Sprengel or Phenol - Sulphonic Acid Method.*

For the direct determination of nitric nitrogen the Sprengel or phenol-sulphonic acid method may be employed. This method, which is a colourimetric one, is very quick, but yields results lower than the truth in presence of chlorides.†

Solutions Required.

(1) *Phenol-sulphonic Acid.*—Melt 18 grms. pure white phenol with 9 c.c. distilled water and add 111 c.c. pure redistilled sulphuric acid ; then digest on water bath for 8 hours at 100° C.

(2) *Potassium or Sodium Hydroxide Solution.*—Approximately 12 N.

(3) *Potassium Nitrate Stock Solution.*—Dissolve 0·722 grm. pure recrystallised potassium nitrate in 1 litre of distilled water. For use, as required, dilute 100 c.c. of this solution to 1 litre with distilled water. One c.c. of this dilute solution is then equivalent to ·00001 grm. Nitrogen.

(4) *Standard Silver Sulphate Solution.*—Dissolve 4·397 grms. of silver sulphate, free from nitrate, in 1 litre of distilled water. One c.c. is equivalent to ·001 grm. Chlorine.

Preparation of Sample.

Should the sample be coloured or possess any turbidity, it must be clarified by aluminium hydroxide as described under chloride determination (p. 35.)

The removal of chloride is also necessary for an accurate determination, although, where the amount does not exceed 3 parts per 100,000 this step may be omitted. It is done by taking a suitable volume of the sample, nearly neutralising with N/10 sulphuric acid, adding sufficient standard silver sulphate solution to precipitate all but about 1 part per 100,000 of chloride and filtering.

Procedure.

An appropriate volume of the sample, 10, 20, or 25 c.c., prepared as above described if necessary, is evaporated on the water bath in a small basin, taking care to remove the basin as soon as the residue is dry. When cold, one c.c. of phenol-sulphonic acid and one c.c. distilled water are added and brought into intimate contact with the contents of the dish. After warming on the water-bath for 10 minutes this is then diluted with distilled water and a moderate excess of caustic potash or soda solution is added.

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* Sprengel, *Pogg. Anal.*, Vol. 121, p. 188 (1864) ; Grandval and Lajoux, *Comptes Rendus*, July 6th, 1885 ; Gill, *Journ. Amer. Chem. Soc.*, Vol. 16, p. 1 (1894).

† Tatlock and Thomson, *Journ. Soc. Chem. Ind.*, 1904, Vol. 23, p. 428. *Cf.* also *Standard Methods of Water Analysis* (American Public Health Association), 5th Edition (1923).

The liquid is then transferred to a Nessler tube, filtered if necessary, made up to 100 c.c., and its colour matched against a standard prepared by evaporating 10 c.c. standard potassium nitrate solution (1 c.c. = ·00001 grm. Nitric Nitrogen), treating this in the same way as the sample.

Approximate Estimation of Nitrate by the Pyrogallic Acid Method.

This colourimetric method was worked out by J. Horsley so long ago as the year 1863 (*Chem. News* for June, 1863, p. 268). The method lays no claim to be perfectly exact, *i.e.*, quantitative, but after a little practice one can arrive in a few minutes at a very fair idea of the amount of nitrate in any given sample, or, at all events, in nearly every sample. The following are the details of the process :—

10 c.c. of the sample, *filtered from all suspended solids*, are poured into a test tube of rather thick glass (a bacteriological test tube 15 c.m. or 6 in. long by 1·25 c.m. or 0·5 in. in diameter), and about 0·2 grm. of pyrogallic acid is dissolved in this and the solution made uniform. After the first two or three trials it is unnecessary to weigh this acid, as it can then be measured out with sufficient accuracy. By means of a small pipette with a bulb at the top and a fine orifice at the outlet, lowered to the bottom of the test tube, 2 c.c. of concentrated nitrate-free sulphuric acid are allowed to flow slowly down on to the bottom of the tube, so as to form a layer below the aqueous one. Before withdrawing the pipette, its upper end must be closed by the finger, in order to prevent the acid still remaining in it from mixing with the aqueous layer of liquid. About 0·1 grm. of *pure dry powdered* sodium chloride (which, like the pyrogallic acid, need only be weighed once or twice) is then dropped into the tube, and falling—as much of it does—on the junction of the sulphuric acid and the water, it gives rise to a brisk effervescence. Should nitrate be present, a purple band forms at this junction, the intensity of the colour produced being proportional to the amount of nitrate.*

A preliminary trial gives a rough idea of this amount, after which a second estimation is made along with three other simultaneous determinations with similar volumes of standard potassium nitrate solution. Thus, if the preliminary trial shows, *e.g.*, about 0·6 part

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* A. Chaston Chapman, in a letter, suggests the following as very possibly indicating the mechanism of this reaction : " Leaving the sodium chloride out of the question for the moment, it is clear that the initial change is one of oxidation, and it is highly probable that in the fairly dilute nitrate layer the pyrogallol is oxidized to purpuro-gallin (pyrogallo-quinone). This is a brown substance which is almost insoluble in water, but dissolves in sulphuric acid, giving a carmine solution. This, in turn, readily becomes purple in the presence of a little nitrous acid. All the conditions necessary for this set of reactions are, I think, realised in the test. If the sodium chloride is really necessary, it may be that the nitrosyl chloride formed would act as the oxidizing agent instead of the nitric acid."

of nitric nitrogen per 100,000 parts of liquid, the three standards are made to correspond to 0·4, 0·6 and 0·8 parts. In this way the nitric nitrogen in the sample may be gauged to within about 0·25 part per 100,000. It is, however, essential that the determinations should be carried out at the same time in both sample and standards, *i.e.*, one following immediately on the other, for it is useless to try to compare two tubes unless they have been prepared within a few minutes of one another ; further, the sodium chloride used must be dry and finely powdered. There is considerable saving of time, in carrying out this test, if a number of dilute standard solutions of nitrate are always kept on hand in stoppered bottles.

The most suitable strength of solution for a determination is about 2 parts nitric nitrogen per 100,000, but estimations can quite well be made down to 0·25 part. It is very rare for a sample of sewage or effluent, even if it should be absolutely devoid of nitrate, to show nothing at all, no doubt because of the charring action of the strong acid upon minute particles of finely divided organic matter still in the liquid. On the other hand, partially purified turbid effluents containing much dissolved or colloidal organic matter usually give readings below the value as determined by the copper-zinc couple method (*cf.* Purvis and Courtauld, *loc. cit.*). If phosphates are present in excess, they interfere with the test by altering the character of the purple band, the results coming out too low.

If nitrite is present in the liquid tested, a yellow colour is produced in the aqueous layer,* but this does not seriously interfere with the nitrate reading unless it is very intense, and in that case standards can be made containing nitrite to the same extent.

NOTE.—It is convenient to have in the laboratory a small leaden tray, large enough to hold a bottle of sulphuric acid and a test tube stand containing a set of tubes, pipettes, etc. If, then, by accident a tube breaks, no harm is done.

E. Ardern and J. Crabtree have made an investigation of this method and their main conclusions are, shortly :—

(1) The pyrogallic acid must be used in accurately measured amounts ; (2) various trials resulted in the choice of 0·04 grm. pyro. and 10 c.c. sample, for general use ; (3) if the nitric nitrogen in the sample does not exceed 0·3 part per 100,000, then a lesser amount (0·02 to 0·03 grm.) of pyro should be taken ; (4) if the sample should be exceptionally rich in nitrate, it is better to dilute it before testing.

PROCEDURE.

Use test tubes, conveniently with a scratch at 10 c.c.
To 10 c.c. of the settled or filtered effluent add 1 c.c. of 4 per cent.

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* This reaction may be made use of to determine *roughly* the amount of nitrite present.

pyrogallic acid solution and pipette 2 c.c. concentrated sulphuric acid gently on to the bottom of the test tube, placing finger on pipette, before withdrawing, to prevent mixing. Then add about 0·1 grm. dry and well-powdered sodium chloride, allow to stand for two minutes and compare with standard tubes :—

Convenient standards are ·1, ·2, ·4 and ·6 part Nitric N per 100,000.

The appended table gives some typical results obtained by them, by this, as compared with the copper-zinc reduction method.

It will be seen that these results leave little to be desired, and they point to the advisability of using the smaller quantities of pyrogallic acid, just mentioned.

Nitric Nitrogen. Parts per 100,000.

Primary Contact Bed Effluent.		Secondary Contact Bed Effluent.	
Pyro.	Reduction.	Pyro.	Reduction.
·18	·12	·66	·71
·42	·58	·84	·61
·12	·13	1·44	1·41
Nil.	·05	1·20	1·34
·12	·02	·42	·50
·15	·03	·96	·85
·15	·28	·48	·44
·15	·10	1·20	·85
·10	·10	1·20	·92
·36	·32	1·56	1·42
·18	·14	·54	·67
·18	·20	·60	·57

Kjeldahl* Process for the Estimation of Total Nitrogen and (indirectly) of Total Organic Nitrogen.

The method to be described below gives a determination at one time of the total nitrogen of a sewage or effluent, and therefore includes :—

(1) The ammoniacal nitrogen ;

(2) The albuminoid nitrogen ;

(3) The nitrous nitrogen ;

(4) The nitric nitrogen ;

(5) The " X " nitrogen, *i.e.*, that portion of the organic nitrogen which is not included in Nos. 1–4 above. This " X "

* For Kjeldahl's original paper, see *Zeitschr. Anal. Chemie*, Vol. 22, p. 366 (1883).

nitrogen, therefore, represents the difference between the total Kjeldahl nitrogen and the sum of the Nitrogens Nos. 1–4 inclusive. The "albuminoid" and "X" nitrogens added together give the total organic nitrogen.

REAGENTS REQUIRED.

(1) *Nitrogen-free Sulphuric Acid.*—It is not always easy to get acid which is quite nitrogen-free. Each half-Winchester of acid used must be tested along with the other reagents of a "Kjeldahl" estimation by making two or three "blank" determinations, *i.e.*, determinations for total nitrogen in the reagents alone, as described below. If these blanks should come out above a certain limit, say, 0·0004 grm. of nitrogen, then the acid should be tested alone for :—

(a) Ammonia, by distilling, say, 10 c.c. in 200 or 250 c.c. of ammonia-free water with excess of ammonia-free potash and nesslerizing the distillate ;

(b) For nitrites, by *m*-phenylene diamine ;

(c) For nitrates, by the copper-zinc couple or other suitable method. If an appreciable quantity of any one of these is found, the acid must be rejected.

(2) *Sugar Solution.*—40 grammes of the purest cane sugar obtainable (small loose crystals, *not* loaf sugar) are dissolved in about 500 c.c. distilled water, and the solution is boiled down in a tinned iron basin with 2 or 3 grammes of stick potash until the volume of the liquid is reduced to about 200 c.c. After cooling, it is made up to about 900 c.c. with ammonia-free water and 100 c.c. of nitrogen-free sulphuric acid are added ; when this mixture is quite cold a little more water is added, to make it up to one litre. 5 c.c. of the final solution therefore contain 0·2 grm. sugar and 0·5 c.c. sulphuric acid. It is a distinct advantage to boil out the sugar with alkali, the "blank" being often appreciably reduced as a consequence. The object of adding the sulphuric acid to the sugar solution is of course to prevent the formation of moulds.

(3) *Strong Potash Solution.*—A pound of stick potash (*i.e.*, 453 grms.) is dissolved in about 1½ litres of distilled water in a tinned iron basin,* the solution warmed to near its boiling-point, and sufficient aqueous permanganate of potash introduced in small portions at a time to destroy any organic matter present. The liquid after prolonged evaporation must still show a slight tinge of green

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* It is a wise precaution to place the tripod which supports the basin in a shallow earthenware crock of suitable size.

manganate when a clean fragment or rod of white porcelain is dipped into it, this small excess of manganate being then finally discharged by the addition of a very little more potash. The solution is evaporated down to about a litre, a little water being *carefully* added (with stirring) from time to time, if required. The amount of permanganate necessary depends, of course, upon the quality of the potash, but each pound of the latter should not require more than about 5 c.c. of saturated aqueous permanganate. The latter is most conveniently added from a pipette, and with a little practice the quantity necessary is arrived at without much trouble. After cooling, the potash solution is siphoned into a Winchester, which should have in it at least two charges of potash ; and it is well to keep two such bottles going, as the manganese mud takes a week or two to settle.* When the supernatant liquid is clear (and colourless), it is again siphoned off into a smaller stock bottle.

(4) *Pure Crystallised Sodium Sulphate.*—This is ground up in bulk and any foreign particles are picked out. Properly speaking, it ought to be recrystallised. Before being ground it is tested for sulphites, thiosulphates, and ammonia (by the Nessler reagent), as these impurities are not unfrequently present in objectionable quantities. It must, of course, contain none of them.†

(5) *Pure Zinc Foil.*—This is cut into strips weighing 3 grammes each, the size of such a strip being about 10 c.m. by 2·5 c.m. These are then boiled out twice with dilute potash (about 3 per cent.), washed thoroughly with distilled water, dried at once, and kept in a stoppered bottle.

(6) *Standard Sulphuric Acid*, approximately deci-normal.

(7) *Standard Alkali* (either potash or ammonia.) This is approximately deci-normal or half deci-normal. The choice of alkali is more or less a personal matter. A solution of ammonia has the advantage of not absorbing carbonic acid to anything like the same extent as potash.

(8) *Sensitive Litmus Solution.*—The directions for preparing this with the use of acetic acid and alcohol are to be found in Sutton's " Volumetric Analysis," 11th edition, p. 34.

Method.—100 c.c. of sewage, or 200 c.c. of effluent, are poured into a round-bottomed flask of resistance glass of about 400 c.c. capacity, the neck of which is roughly 12 cm. long and 2 to 3 c.m. in diameter ; 5 c.c. of the sugar solution, 0·5 c.c. nitrogen-free sulphuric

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* This manganese mud is free from nitrogen.

† It would save trouble to add the sodium sulphate in the form of solution, after the liquid in the *Kjeldahl* estimation had been reduced to about 20 c.c., but this lengthens the process appreciably.

acid and a 3-gramme strip of zinc are then added, and the mouth of the flask is covered with a pad of moistened cotton wool interposed between two or more layers of clean filter or tissue paper, the overlapping ends of which are preferably kept tight by a rubber band. The flask is then set aside in a slightly inclined position. A number of such flasks are conveniently placed along a shelf, each one being loosely gripped by a small steel clip screwed on to a horizontal spar of wood. The above method of protecting the liquid was adopted as the result of experience, for it was found that distilled water exposed to the air absorbed very appreciable quantities of ammonia.

A further addition of 0·5 c.c. sulphuric acid is made each day until the zinc is entirely dissolved, this usually requiring five days. *The above slow addition of acid and slow reduction are essential*, for we have found that if the reduction of a nitrated effluent is hurried, there will almost certainly be a loss of nitrogen and the estimation will come out too low. The cotton wool protection having been finally removed, the acid in the flask (inclusive of the 0·5 c.c. contained in the added sugar solution) is then made up to 10 c.c. in all, and evaporation, preferably on wire gauze over a rose burner, or even over a naked flame, is commenced (this has, of course, to be done in a draught cupboard, the flask being well inclined). Frothing takes place when nearly all the water has been evaporated off, and hence the flask requires watching at this stage. As soon as bumping begins, the flask is allowed to cool, 8 grammes of the powdered sodium sulphate are added, and the flame is again applied. When the water of crystallization of the sodium salt has been driven off, the acid begins to fume, and the neck of the flask must now be virtually closed by a small glass balloon which fits fairly closely ; heating is then continued until the contents of the flask are colourless, or only faintly yellow, this last stage usually requiring from two to three hours.

After the flask has cooled down, the cake of sulphates is dissolved in ammonia-free water and the solution is transferred to the distilling flask, A (see fig. 1), this latter being also preferably of resistance glass, round-bottomed, and of 750 to 1,000 c.c. capacity. Three or four pieces of wrinkled-up platinum foil* are added, to prevent bumping during the distillation. This flask is then connected by a stout rubber joint to a small Liebig's condenser, C, an anti-spit apparatus, such as a Travers' adapter, B, being interposed between flask and condenser, so as to avoid the possibility of any alkali being carried over mechanically. The inner tube x of the condenser C projects about 15 to 18 c.m. beyond the lower end of its water jacket, and is bent at such an angle as to be vertical when the condenser is in

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* For a long time fragments of granulated zinc were used for this purpose. But there must have been a little hydrogen produced by the action of this zinc on the dilute alkaline solution in the distilling flask, and this hydrogen would exert a reducing action upon any traces of nitrate present in the permanganated potash. A minute error might thus be introduced into the estimation, though of course the conditions when distilling both estimation and blank were as nearly as possible the same.

position. The distillate is collected in the two flasks, D and E (of 500 and 100 c.c. capacity, respectively), fitted together in the usual way by tubes and rubber stoppers, while at the outlet of E there is a small glass tube or tower, F, containing moistened fragments of broken glass. Tube x is not allowed to dip into the distillate, even at the end of the operation, in order to avoid all chance of the liquid being sucked back into the distilling flask.
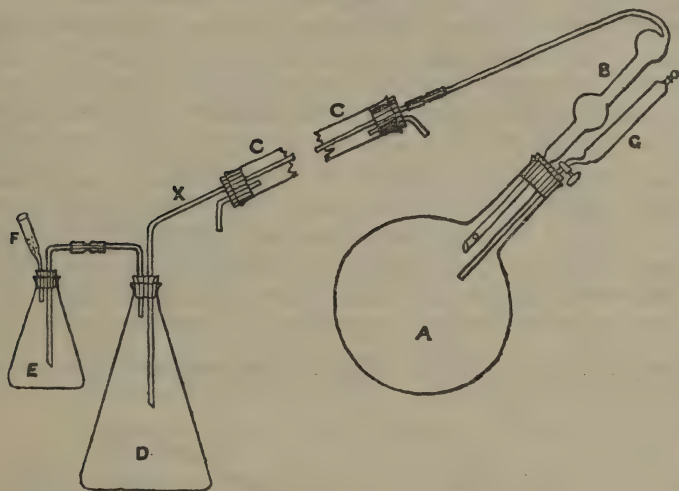
FIGURE 1.

Before the receiving flasks are fitted on, an amount of the deci-normal acid, more than sufficient to neutralise all the ammonia in the distillate, is measured into D from a burette, while E receives about 0·5 c.c. and F a few drops, the total volume of acid used being then read off and noted. When all the connections have been made, the requisite excess of purified potash (*i.e.*, about 2 c.c. more than would be required to neutralize 10 c.c. of the nitrogen-free sulphuric acid) is run into A through a long tap funnel G, which is then rinsed with a little water, and distillation is carried on until bumping commences. At this stage about 30 c.c. of ammonia-free water are run in, and distillation is continued until the flask begins to bump again, when the operation is stopped. The whole distillation takes from three-quarters of an hour to one hour ; it is a distinct advantage, as regards time, to wrap cotton wool round the neck of the flask and the adapter, but this must not be placed sufficiently near the flame to catch fire.

The contents of F and E are now rinsed into the larger Flask D, and a few drops of litmus solution are added. The carbon dioxide present is then boiled off, the flask cooled in water, and the residual acid determined by titration with the standard alkali in the ordinary

way. A simple calculation then suffices to give the ammonia found in terms of *Total Nitrogen* per 100,000 parts of sewage or effluent.

<div align="center">" BLANKS."</div>

As already indicated on p. 20, it is necessary to make two or three blank experiments for each set of reagents, using 200 c.c. of distilled water in place of the sewage or effluent. In those " blanks " the quantities of reagents used and the whole procedure—including the length of time occupied in dissolving the zinc—should be exactly the same as given above. Occasionally, when pressed for time for the figure of a " blank," the process has been quickened, the tendency has been for the result to come out too low.* The volume of deci-normal acid required to neutralise the distillate of a blank estimation should not exceed 0·2 c.c. ; we have, in fact, had it as low as 0·11 c.c.

A part of the above " blank " no doubt comes from the alkali of the upper heated portion of the glass tube x through which the water distils ; hence it is important to shorten the time of distillation as much as possible, *e.g.*, by using a thin condensing tube of hard glass, which allows of quicker distillation than a thick one does. A silver tube, bent into the Adapter shape (Fig. 2) is even better.†

A very small part of the " blank " also no doubt arises from the

<div align="center">FIGURE 2.</div>

solvent action of the slightly acid liquid upon the glass of Flask D, when carbonic acid is being boiled off towards the end of the titration.

The use of sugar as an additional reducing agent to the zinc foil was determined upon after a considerable amount of time had been spent in experimenting with other substances usually recommended for this purpose, *e.g.*, zinc dust, salicylic acid, etc. ; but the " blanks " given by these latter were much too large for this delicate nitrogen determination. The following series of duplicate determinations of the total nitrogen in various kinds of effluents, *with and without sugar*,

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* Thus, a slow " blank " done upon reagents which were not very pure, gave nitrogen equivalent to 0·45 c.c. standard acid, while a " quick " blank showed only the equivalent of 0·29 c.c.

† Thus the following blanks were obtained with the same set of reagents :—
Silver tube : 0·08 c.c. and 0·08 c.c. acid = 0·00011 grm. nitrogen.
Glass tube : 0·14 c.c. and 0·12 c.c. acid = 0·00019 grm. nitrogen.

by the same experimenter, appear to show, however, that reduction with zinc and acid alone is sufficient :—

| No. of Sample. | Nature of Sample. | Nitrogen—Parts per 100,000. | | Difference. |
		With Sugar.	Without Sugar.	
No. 159	3rd Field effluent	1·88	1·54	— 0·34
,, 168	Final filtration effluent ..	0·64	0·60	— 0·04
,, 169	Final irrigation effluent ..	1·30	1·48	+ 0·18
,, 183	1st Field effluent	9·36	9·38	+ 0·02
,, 185A	1st Field effluent	10·11	10·32	+ 0·21
,, 187B	1st Field effluent	8·08	8·13	+ 0·05
,, 188	1st Field effluent	6·92	6·88	+ 0·04
,, 189c	2nd Field effluent	6·22	6·26	+ 0·04
,, 192	2nd Field effluent	5·63	5·61	— 0·02
,, 199	1st Field effluent	4·90	4·53	— 0·37
,, 204	General filtration effluent	1·91	1·90	— 0·01
,, 205	General filtration effluent	1·82	1·80	— 0·02
,, 205c	Filtration effluent	1·51	1·52	+ 0·01
,, 207	Filtration effluent	2·82	2·78	— 0·04
,, 209	Filtration effluent	1·90	1·90	± 0·0

It will be seen from this table that the total quantity of nitrogen in the above effluents varied between 0·60 and 10·32 parts per 100,000,—a wide range ; further, much of the nitrogen was in the form of nitrate. In eleven of the above fifteen duplicate estimations the difference is only in the second decimal figure, and never above 0·05 ; in the other four cases, whether owing to errors of sampling or of analysis, the agreement is not so good. But the foregoing figures are sufficient to prove the consistency of the results obtained by this modification of the *Kjeldahl* method, while at the same time they indicate that the use of the sugar solution might possibly be dispensed with in the case of effluents, and therefore also in the case of sewages and tank liquors. One advantage of not using sugar is that the time required in the final heating of the sulphates in the Kjeldahl flask is shortened, and this of course lessens any possible chance of traces of ammonium sulphate being carried away mechanically by the escaping sulphuric acid fumes. On the other hand, an effluent might conceivably, though not probably, contain a nitrogenous compound not reducible by zinc and acid alone (*cf.* Dyer, *Journ. Chem. Soc.* for 1895, p. 811). In the paper just cited, Dyer gives a very full list of substances which yield up all their nitrogen under the Kjeldahl process which he followed.

To sum up shortly :—This slow reduction Kjeldahl method, if carried out in the manner detailed above, is excellent for arriving

directly at the total nitrogen in a sewage, tank or precipitation liquor, or effluent. It is also to be recommended for the *indirect* determination of the " x " nitrogen and the total organic nitrogen in sewages, tank or precipitation liquors, and (with care) in effluents of average quality. But with very pure effluents, whose nitrogen is present almost altogether as nitrate, the errors of experiment are too great for this indirect method for the determination of " x " nitrogen and total organic nitrogen to be of value. When once the details of the process have been mastered, it does not require a disproportionate amount of time to carry it out. Besides the information which it gives as to the composition of the liquid in question, it acts as a check upon the other figures of analysis.

For the influence of nitrites and nitrates on the foregoing Kjeldahl method, see Appendix 4.

Kjeldahl Processes for the Direct Estimation of Total Organic Nitrogen.

(1) This process, as given by the American Public Health Association in their " *Standard Methods for the Examination of Water and Sewage,*" 5th Edn., pp. 17–18, is as follows :—

The Kjeldahl method of determining organic nitrogen effects the complete destruction of organic matter, with conversion of all nitrogen to ammonia . . . . . .

Procedure.—Boil 500 c.c. of the sample in a round-bottomed flask to remove ammonia ; this usually causes the loss of 200 c.c. of the sample, which may be collected for the determination of ammonia nitrogen. Add 5 c.c. of nitrogen-free concentrated sulphuric acid and a small piece of ignited pumice. Mix by shaking. Digest under a hood until copious fumes of sulphuric acid are given off and the liquid becomes colourless or a pale straw colour. If necessary, the digestion temperature may be raised by addition of 5 grammes anhydrous potassium or sodium sulphate. Cool. Dilute to 300 c.c. with ammonia-free water. Make alkaline with 10 per cent. ammonia-free sodium hydrooxide. Distil the ammonia and complete its estimation either by :—

(*a*) Nesslerizing ;

or (*b*) Titration with standard acid.

(2) Fowler (*Sewage Works Analysis*, pp. 58–60 (1902) carries out the process as follows :—

About 30 c.c. of the sewage or tank liquor may be conveniently taken. This, after a small addition of sodium carbonate, is distilled with steam until the distillate shows no indication of free ammonia. During the progress of the distillation the sample is concentrated to about 5 c.c. This is then transferred to an 8 oz. resistance flask with a long neck, 20 c.c. of nitrogen-free sulphuric acid are added, and

the mixture is heated carefully over the bare *Bunsen* flame for about half-an-hour in a good draught cupboard. A little phosphoric anhydride is then added and the mixture is heated further until it becomes quite clear. After being allowed to cool somewhat, it is poured into about 200 c.c. of ammonia-free water and, after complete cooling, this is made up to 250 c.c. 50 c.c. of this solution are then taken and made alkaline with a saturated solution of caustic soda, 500 c.c. of water are added and the ammonia is distilled off and nesslerized in lots of 100 c.c.

In this case, also, a corresponding blank determination must be made on 35 c.c. water plus the various reagents.

The ammonia found, less the ammonia of the blank, represents only the organic nitrogen of the sample.

(3) In the work of the Royal Commission on Sewage Disposal some experiments were made on the determination of the organic nitrogen *without reduction*. (*cf. Royal Commission on Sewage Disposal*, 4th Report, Vol. IV, Part V, pp. 35–37). From 10 to 100 c.c. of the sample (according to its strength) were boiled down with 4 c.c. of nitrogen-free sulphuric acid in a round-bottomed resistance flask, the heating being continued, after all the water had been evaporated, until the acid became colourless ; the mouth of the flask was closed by a small glass balloon as soon as the acid began to fume. After dilution and, sometimes, after precipitation of the lime present with oxalate of potassium, the clear liquid was nesslerized.

A corresponding " blank " estimation was also made.

The figure obtained represented the Ammoniacal + Organic Nitrogen of the sample.

These experiments, however, showed certain discrepancies, which appeared to be caused by the presence of nitrate, and this was confirmed by making some " Kjeldahl " estimations of water containing from 2 to 10 parts of nitric nitrogen per 100,000. It was then found that the greater part of the nitric nitrogen persists in the sulphuric acid solution until shortly before the latter begins to fume. The free nitric acid, which is then of course concentrated, must exert an oxidizing action upon any organic matter present, some of the organic nitrogen being then probably lost in the form of lower oxides of nitrogen.

L. Whipple, however, in a paper on the Determination of Organic Nitrogen in Sewage by the Kjeldahl Process (*Massachusetts Institute of Technology, Contributions from the Sanitary Research Laboratory and Sewage Experimental Station*, Vol. IV, p. 162 (1908)) ; *Studies on Direct Nesslerization* ; gives details of a method of direct nesslerization by which he claims that accurate results can be obtained.

CONCLUSION.

The appropriate conclusion, therefore, appears to be that the *direct* determination of Ammoniacal + Organic Nitrogen or of

Organic Nitrogen alone, *without reduction*, is applicable in the case of sewages and tank liquors generally, but not always in the case of effluents. For these, the method *with slow reduction* should be followed. For an interesting and exhaustive paper on the subject, *cf.* E. B. Phelps, *Massachusetts Institute of Technology, Contributions from the Sanitary Research Laboratory and Sewage Experiment Station,* Vol. I, p. 101 (1905).

"Oxygen Absorbed" from a solution of Acid Permanganate at 26·7° C. (80° F.) :—(a) in 3 minutes ; (b) after four hours.*

The principle of this well-known test is sufficiently explained by its title.

SOLUTIONS REQUIRED.

(1) *Aqueous potassium permanganate,* containing 0·394 grammes K MnO$_4$ per litre.

(2) *Dilute sulphuric acid,* permanently tinted with N/80 permanganate, *i.e.,* 3 vols. water and 1 vol. concentrated acid.

(3) N/40 *Sodium thiosulphate,* containing about 6·2 grammes of the salt and 1 gramme of sodium carbonate or 10 c.c. of N/1 NaOH per litre.

The oxygen value of this thiosulphate is determined by means of deci-normal bichromate solution (prepared from the re-crystallised and pure salt), potassium iodide and hydrochloric acid (chlorine-free), as given in Sutton's " Volumetric Analysis," 7th edition, p. **131.** This value should of course be frequently checked, as the solution tends to weaken with time ; and, for the same reason, its equivalent of permanganate should be determined for each day that it is used.

(4) *A dilute and clear solution of Starch.* This must not contain any floating particles.

To enable the starch indicator to keep for a month, a little caustic soda solution is added (to 5 grms. of starch add 20 c.c. of 1 per cent. NaOH per litre). It is, however, better to renew the starch solution very frequently, even daily, in warm weather.

PROCEDURE.

The permanganate and sulphuric acid are measured into a glass-stoppered bottle of about 200 c.c. capacity and the bottle is then

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* Forchammer, *Brit. Assoc. Report* for 1849, Abstracts, p. 37 ; Tidy & Letheby, *Journ. Chem. Soc.* for 1879, p. 66.

carefully warmed to a temperature of 26·7°C. A portion of the sample of sewage liquor or effluent is warmed separately to the same temperature and the requisite quantity of it is then added to the acid permanganate, the contents of the bottle being mixed by gentle rotation. After 3 minutes or 4 hours, as the case may be, the liquid is cooled down quickly, 10 c.c. of 5 per cent. potassic iodide solution or a few crystals of the pure salt are added, and the liberated iodine is titrated with standard thiosulphate, a few drops of the dilute starch solution being added towards the end of the reaction.

A blank test should be made each day.

If the sample contains nitrite, this should be estimated and the necessary correction made, if so desired.

For both the 3 minutes and the 4 hours' tests, not less than 10 c.c. nor more than 100 c.c. of the sample should be taken, the amount varying from 10 c.c. in the case of a very strong sewage or trade effluent to 100 c.c. in the case of a good filter effluent ; 10 c.c. of acid are added, followed by 50 c.c. of permanganate, the volume being finally made up to 160 c.c. with distilled water.

The Mersey and Irwell Joint Committee have found it convenient to use the following proportions :—

For Good, Fair and Unsatisfactory Effluents.	For Bad Effluents.		For Sewage Liquors.
70 c.c. Effluent	70 c.c. Effluent	or { 25 c.c. Effluent 45 c.c. Distilled Water	An aliquot part of the sewage liquor to be taken and diluted to
50 c.c. Permanganate	100 c.c. Permanganate	50 c.c. Permanganate	70 c.c., such that not more than 50 % of the
10 c.c. (25 %) Acid	20 c.c. Acid	10 c.c. Acid	permanganate shall be consumed ; the 3
Equivalent to Oxygen supplied :—			minutes' preliminary test being taken as a
7·14 parts per 100,000	14·28 parts	20 parts	guide for this.

These quantities will leave, on the average, at least 50 per cent. of the available permanganate oxygen unconsumed; it is of course always desirable to have a large excess of permanganate present. In the 4 hours' test it may be advisable to rotate the contents of the bottle gently at the end of the first hour—this, more especially, when the sample contains appreciable solid matter.

There are a considerable number of analytical records (including those of the Royal Commission on Sewage Disposal) in which the foregoing " Oxygen Absorbed " test has been made with N/8 permanganate (3·94 grms. $KMnO_4$ per litre) and at 26·7°C

Broadly speaking, between this and the test with N/80 perman-
ganate at approximately laboratory temperature, the following
ratio appears to hold fairly regularly, especially with regard to
sewages and tank liquors :—

	N|80 Permanganate, 4 hrs. at approx. 18·3° C.	N|8 Permanganate, 4 hrs. at 26·7° C.
Ratios of " Oxygen absorbed "	1·0 :	1·6

But this is merely mentioned here as giving a rough guide when
it is a question of interpreting different records.

Incubator Test (by Permanganate).

This is carried out, as recommended by Mr. Scudder, as follows :—

A small well-stoppered bottle (of about 125 c.c. capacity) is
completely filled with effluent, the stopper firmly inserted, and the
liquid incubated at a temperature of 26·7° C. (80° F.) for five days.
At the end of this time the " oxygen absorbed " from permanganate
in 3 minutes is again determined. If either the same quantity of
permanganate or less of it is now required than in the corresponding
estimation on the original sample, the liquid has withstood incu-
bation ; if, on the other hand, more is needed, it has not. In working
out the quantities of permanganate oxygen thus used, allowance
must be made for the nitrite present ; *i.e.*, the amount of oxygen
equivalent to the nitrous nitrogen in the solution at the time of the
thiosulphate titration is deducted from the total permanganate
oxygen used up. The reason for this, of course, is that, although
nitrites are themselves readily oxidized by permanganate, they are
on the other hand oxidizing agents as regards organic matter
generally.

Incubator Test (by Smell).

A much simpler form of incubator test than the above consists
in merely noting the appearance and smell of the liquid after in-
cubation. If the sediment has become dark coloured (from the
formation of sulphide of iron), the smell is invariably putrid, whereas
if it remains brownish-red, the liquid is usually quite inoffensive.
On the whole, the permanganate incubator test is the more stringent
of the two.

Occasionally, though not often, a case arises where the charac-
terisation of the smell is for one reason or another difficult, this being
not infrequent when nitrite in considerable quantity is produced
during the incubation. Doubtful cases can, however, often be
resolved by testing the air in the upper part of an incubation bottle
with a strip of *slightly* moistened acetate of lead paper, after shaking
up the liquid. On the whole this test is of great practical value
because of its simplicity.

Note.—It sometimes happens that five days' incubation at 80°F.
is not sufficient to indicate offensive putrefaction, an effluent
occasionally remaining sweet for five days, but becoming bad if

incubated for a longer period. But, for all practical purposes, five days may be taken as long enough.

A Proposed Alternative Incubator Test.

The Committee of the Association of Managers of Sewage Disposal Works would urge that consideration be given to the advisability of a change in the incubator test, in the direction of shortening the time of incubation and raising the incubation temperature. Within limits, the incubator test affords valuable information to sewage chemists, especially as a control ; but its usefulness is greatly reduced by the long delay in obtaining a result. The Committee feel that if the test were shortened to a period of 48 hours' incubation at a slightly higher temperature, it would be of much more use than it now is. In a number of experiments which have been carried out, it has been found that 2 days' incubation at 37°C. yields much the same results as 5 days' incubation at 27°C., and it is felt that alteration of the test to the shorter incubation period would be an advantage. The short period incubation at 37°C. is slightly more stringent than the existing test.

Stability Tests.

(1) **F. Scudder's Qualitative Method for Dissolved Oxygen Absorption by Sewages and Sewage Effluents.** (See Fifth Report, *Royal Commission on Sewage Disposal*. Appendix I. Minutes of Evidence (Cd. 4279), p. 684.)

SOLUTIONS REQUIRED.

(1) Indigo carmine solution. 2 grms. per litre.
(2) Sodium Bicarbonate solution. Saturated solution.
(3) Sodium Hydrosulphite solution ($Na_2S_2O_4$).* This is prepared just before using by adding 1 to 2 grms. of solid sodium hydrosulphite to 30 c.c. of the saturated sodium bicarbonate solution.

The apparatus is assembled as shown in Figure 3.† A is filled to within ½-in. of the top with the indigo carmine solution, B is half filled with dilute hydrochloric acid (1 vol. acid + 2 vols. water), and C is filled with the sodium hydrosulphite solution. The syphon is best made with water before assembling the apparatus. To get rid of the oxygen in the hydrogen generator, the latter is slightly lifted off the ground joint, when the acid rises in the generator and hydrogen is evolved. In about half a minute it can be replaced in its position, as the air will now have been displaced by hydrogen. Sodium hydrosulphite solution can then be run in in small quantities until the blue

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* *Note.*—This compound can now be bought. For details of its preparation, *cf.* Scudder, *Royal Commission on Sewage Disposal*, 5th Report, Appendix VII, p. 38 [Cd. 4285].

† *Note.*—A has a capacity of about 250–300 c.c. ; B a capacity of 30 c.c. without the tube containing the zinc (about 15 c.c. of acid are sufficient) ; and C a capacity of 15 c.c.

indigo solution turns yellow. As there will be air still left in the apparatus, the surface of the reduced indigo will turn blue, when a little more hydrosulphite solution can be added and the whole gently shaken. After this operation has been repeated a few times, the reduced indigo will remain a clear yellow.
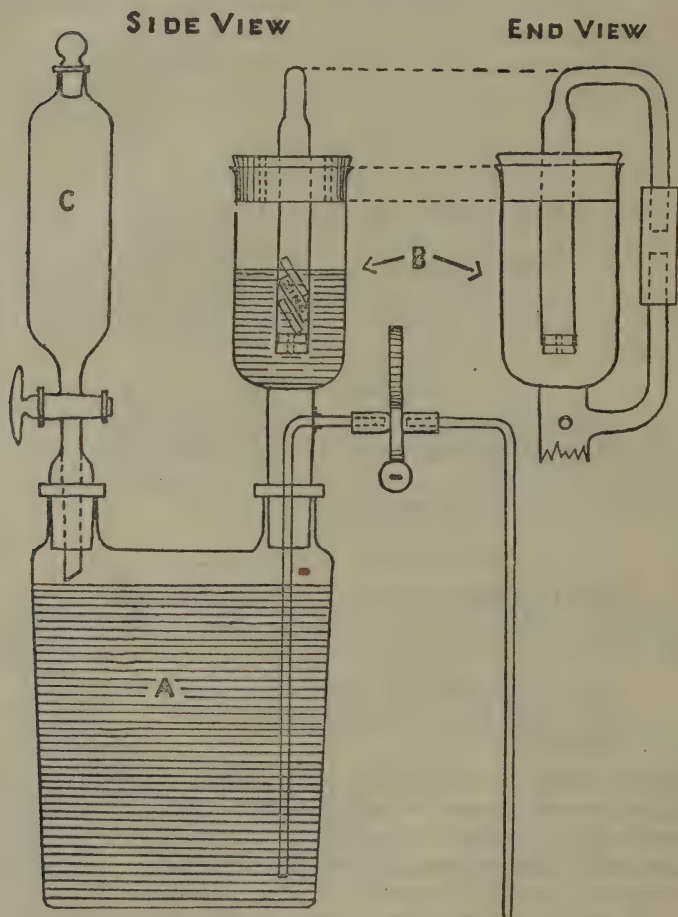
Fig. 3—F. Scudder's Reduced Indigo Apparatus.

The reaction when the solid hydrosulphite dissolves in water is probably :—

$$Na_2S_2O_4 + H_2O = NaHSO_2 + NaHSO_3.$$
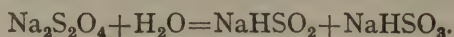
Procedure.—240 c.c. of the sample and 300 c.c. of tap water (*i.e.*, dilution 4+5), of temperature 14·5°C., are shaken together in a Winchester quart bottle for 2 minutes, and allowed to stand for a further 2 minutes, to allow the air bubbles to escape. 4 bottles as shewn in Figure 4), each having a capacity of 110 to 120 c.c.,

are then filled (gently and without splashing), stoppered (as per figure) and incubated at 18·3° C. One bottle is taken out after 2 days and tested for dissolved oxygen in the following manner. The stopper is gently removed, the syphon of the indigo apparatus introduced a little way into the bottle and the pinchcock opened to allow a little reduced indigo to flow in. If any oxygen is left in solution the reduced indigo added will immediately turn blue, but if there is none left it will remain yellow. The remaining bottles are taken out after 3, 4 and 5 days respectively.
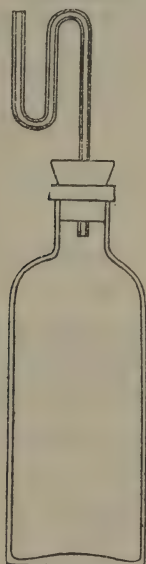
Fig. 4—Bottle used for Indigo Carmine Dissolved Oxygen Test. Capacity, 110 to 120 c.c.

(*N.B.*—It is best before making a test to run a little reduced indigo to waste, to make sure that there is no blue indigo solution in the syphon, due to oxygen having diffused through the rubber.)

Aerated water and sewage effluents at 14·5°C. should contain 7 c.c. of oxygen per litre or 0·7 grain of oxygen per gallon (=1·0 part by weight of oxygen per 100,000). Therefore, an aerated mixture of sewage effluent and water in the ratio of 1+1 should present to the effluent 1·4 grains of oxygen per gallon or 2 parts of oxygen per 100,000. In the case of good or fair effluents this is sufficient for the purpose, but in the case of unsatisfactory or bad effluents, the oxygen supplied is too low.

By adopting a dilution of 4+5 the errors are more evenly balanced, *i.e.*, the oxygen supplied to good or fair effluents is slightly greater than 1·4 grains per gallon or 2 parts per 100,000, and with unsatisfactory and bad effluents the average results are approximately correct. The accompanying table will make matters clear.

Comparison of the amounts of dissolved oxygen to be presented to the sewage effluent, using dilutions of 1+1 and 4+5.

Results in Parts per 100,000.

Dilution	1 + 1		4 + 5	
Oxygen presented to effluent.*	For samples classed as good or fair.	For samples classed as unsatisfactory or bad.	For samples classed as good or fair.	For samples classed as unsatisfactory or bad.
Theory ..	2·01	2·01	2·26	2·26
Highest ..	2·07	2·04	2·27	2·09
Lowest ..	1·70	1·46	1·81	1·70
Average ..	1·90	1·80	2·09	1·97
Error on Royal Commission Standard of 2·0.				
Highest ..	+·07	+·04	+·27	+·09
Lowest ..	—·30	—·54	—·19	—·30
Average ..	—·10	—·20	+·09	—·03

Table showing variation in the amount of Dissolved Oxygen presented to the effluent when the temperature of aeration is above 14·5°C. Calculated from Roscoe and Lunt's table.

Parts per 100,000.

Temperature °C.	Dilution 1+1.	Dilution 4+5.
14·5	2·01	2·26
15	1·99	2·24
15·5	1·97	2·21
16	1·95	2·19
16·5	1·93	2·17
17	1·91	2·15
17·5	1·89	2·12
18	1·87	2·10
18·5	1·85	2·08
∴ 18·3	1·86	2·09

(2) Methylene Blue Stability Test.

In the United States the time required for the decolourization of Methylene Blue by an effluent on incubation is used as a measure of its stability. The *Procedure* is given in the American Public

* NOTE.—The figures given in this table are actual determinations of the oxygen presented to the effluent at start. They cover the results obtained from a long series of tests made in order to ascertain the most suitable dilution to be employed.

Health Association's *Standard Methods of Water Analysis*, and this is based on the two following papers :—

(1) E. B. Phelps, " Putrescibility and Stability of Sewage Effluents." *Contrib. Sanit. Research Lab., Mass. Inst. Tech.*, Vol. V, pp. 74–88 (1909) ; and

(2) A. Lederer, " A Serious Fallacy of the 'Standard' Methylene Blue Putrescibility Test." *Amer. Journ. Pub. Health,* 4 (Old Series 10), pp. 241–8 (1914).

Determination of Chlorides.

Solutions Required.

$\left(\text{These are approximately } \dfrac{N}{35}\right)$:—

(1) *Silver Nitrate*.—4·79 grms. of the dry crystallized salt per litre. 1 c.c. of this solution is equivalent to 0·001 grm. chlorine.

(2) *Sodium Chloride*.—1·648 grms. of the pure dry salt per litre. 1 c.c.=0·001 grm. chlorine.

This sodium chloride is conveniently prepared by making a strong solution of ordinary table salt, allowing this to stand overnight, and then filtering it clear. Hydrochloric acid gas (from salt and sulphuric acid) is then passed into the aqueous solution through a tube which is not too narrow, and which is widened to a kind of small funnel at the end which dips into the salt solution. As the latter becomes acid, sodium chloride begins to crystallize out in small crystals. The magma thus obtained is drained by the pump through a funnel stopped by a platinum cone, washed once or twice with small quantities of water, and finally ignited gently in a platinum basin. Pure sodium chloride may also be purchased.

(3) *Neutral Chromate of Potassium* (K_2CrO_4). 50 grms. of the pure salt are dissolved in a little distilled water and sufficient silver nitrate is added to produce a slight red precipitate. After standing for one or two days this is filtered off and the filtrate made up to one litre with distilled water.

(4) *Aluminium Hydroxide*.—Dissolve 125 grms. of potash or ammonia alum in a litre of distilled water, precipitate the alumina by the cautious addition of ammonia, and wash the precipitate until it is free from chloride, nitrite, nitrate and ammonia. Make up the mixture of hydroxide and water to one litre.

If the sample of effluent should be distinctly coloured, it can be conveniently decolourized by shaking it up with a little of the aluminium hydroxide water (about 1 c.c. of the latter to 150 c.c. of the sample), allowing to settle and filtering if necessary.

If the sample is acid, it should be neutralized with calcium

bicarbonate or with sodium carbonate; if alkaline to phenol-phthaleïn, dilute sulphuric acid should be added until the colour is just discharged.

If sulphides are present to the extent of ·4 part per 100,000, or over, a slight excess of powdered zinc sulphate should be added to about 100 c.c. of the sample and, after filtering, the estimation of the chlorine proceeded with.

As thioycanates give a white precipitate with silver nitrate, they should, if present, be estimated colourimetrically with ferric chloride or sulphate and the necessary correction made.

The silver nitrate solution is first standardized against the solution of sodium chloride, evaporated down as in an actual estimation, using the chromate as indicator. A number of such estimations made with two different silver solutions against new standard sodium chloride gave results practically agreeing with one another, the average value of 1 c.c. of silver nitrate, in terms of chlorine, being 0·000995 grm. (instead of 0·001 grm.).

Process.—In an actual estimation 50 c.c. of the filtered sewage or effluent are evaporated* down to a volume of 1 or 2 c.c. (or even to dryness, if the titration has to be delayed), in a porcelain basin on the water bath. A few drops of the chromate solution are added to this residue, which is then titrated with the solution of silver nitrate under constant stirring, the end of the reaction being marked by the persistence of the colour of the orange-red silver chromate. This plan of evaporation before titration is adopted because, when working with a pure dilute solution of sodium chloride, it was found that more than the theoretical quantity of silver nitrate had to be added before the indicator marked the end of the reaction, this excess being greater with high dilutions of the chloride.† It is thus desirable that the volume of the chloride solution to be titrated shall not exceed one and a half times the volume of the silver nitrate required, if this excess is to be avoided. It would not of course do to evaporate an acid sewage or effluent without first rendering it slightly, but distinctly, alkaline with a solution of pure bicarbonate of lime, bicarbonate of soda, or carbonate of soda, neutralizing in the case of the sodium salt any excess of alkali with nitric acid after the evaporation and charring.

In order, however, to save the time and trouble involved in evaporating 50 c.c., the solution of silver nitrate might be standardized against 50 c.c. of standard dilute sodium chloride solution. This method is perhaps sufficiently accurate for most purposes. Any small experimental error arising from the solubility of silver chromate need not be taken into account.

The organic matter in a filtered sewage, tank liquor, or effluent must exert some slight reducing action upon the silver solution used,

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* This evaporation must be done in a draught cupboard, to prevent the escape of ammonia into the air of the room.

† Cf. Dittmar, " Quantitative Chemical Analysis," pp. 219-220.

and to get an absolutely correct estimation of the chlorine present would necessitate the destruction of all organic matter. In actual practice, however, this has been found to be unnecessary. To ascertain the extent to which the results are affected by the organic matter, a number of comparative estimations of chlorine were made in different ways (*i.e.*, gravimetrically as silver chloride; by direct titration without evaporation; direct-titration after evaporation; evaporation with charring; evaporation with sodium carbonate and charring; evaporation with calcium bicarbonate and charring). The results obtained are given in the 4th Report of the Royal Commission on Sewage Disposal, Part V., pp. 43–44. From those results the conclusion was drawn that, within the limits of accuracy necessary here, the organic matter in solution in a filtered sewage, tank liquor or effluent, which has been concentrated by evaporation, does not sensibly reduce silver nitrate during the short time required for the titration of the chloride present.

NOTE.—A solution of bicarbonate of lime is a very useful form of base for preventing loss of chloride during the evaporation of such solutions as the above, and the subsequent charring of the residue. The excess of lime helps to keep the residue porous, and as it is finally left in the state of normal carbonate it is readily filtered from the aqueous solution; further, this solution can be titrated direct with silver nitrate, *i.e.*, it does not require the addition of any nitric acid.

Alkalinity and Acidity.

The determination of alkalinity and acidity calls for some comment in regard to the expression of results, as on this point considerable diversity of opinion exists. Thus, the West Riding of Yorkshire Rivers Board, in their report on Methods of Analysis in their own laboratory, say :—

"When it is evident that the alkali is chiefly present as carbonate, the result as given by the methyl orange test is set down in terms of Na_2CO_3, $CaCO_3$, or NH_3, whichever is likely to be present. When, on the other hand, the alkali is chiefly present in the free state, the result as given by the phenolphthaleïn test is set down as $NaOH$ or CaO."

The American Public Health Association in their report say :—

"Results . . . . may be given as phenol-phthaleïn alkalinity and methyl orange alkalinity, substituting for those names the names of other indicators, if others are selected; or the results may, in cases when the alkalinity is due to bicarbonate, carbonate, and hydroxide, be calculated to these radicles."

Other authors and authorities have different methods of expression.

Having regard to the present diversity, and to the fact that we are dealing solely with sewage and sewage effluents (although these

may contain trade wastes), it is recommended that results be set down as alkalinity (or acidity) in terms of H_2SO_4. Uniformity of expression would simplify comparison of different sewages, and expression in this form would make it a simple matter to convert to terms of various alkalies for special purposes, if required.

Method.—50 to 100 c.c. of the sample are titrated with $\frac{N}{10} H_2SO_4$ for alkalinity, using phenol-phthaleïn and methyl orange or methyl red as indicators. For acidity, $\frac{N}{10}$ NaOH should be used, with methyl orange as indicator. The results would be set down as " alkalinity to phenol-phthaleïn " and " alkalinity (or acidity) to methyl orange or methyl red."

A sensitive solution of litmus is also convenient for certain titrations.

For further consideration of the subject, the reader is referred to Ostwald's *Foundations of Analytical Chemistry*, 3rd English edition, p. 127, *et seq.* ; Prideaux' *The Theory and Use of Indicators* (1917) ; and to the American Public Health Association's *Standard Methods for the Examination of Water and Sewage*, 5th edition, p. 32, *et seq.*

In cases of strong and coloured sewages where the end point is difficult to detect, and for routine work where a large number of samples is involved, it will generally be sufficiently accurate to take a larger quantity of the sample and use $\frac{N}{1}$ acid or alkali, thereby obtaining a quicker end point.

Hydrogen Ion Concentration.*

Although the determination of hydrogen ion concentration is not likely to become a routine test at present, there are occasions when its employment is of the greatest value, for example, in problems connected with the dewatering of activated sludge, in investigations of the most favourable conditions for sludge digestion, and in various other respects.

There are two methods at present in use for this determination, the electrometric and the colourimetric methods. The American Public Health Association, after comparison and consideration of the two methods, state that " colourimetric methods which depend upon the use of indicators, whose colours in solution are characteristic of the hydrogen ion concentration of the solution, are considered more satisfactory for most control and research problems in water work." There is little doubt that the colourimetric method is the quicker of the two and therefore for routine work has a decided advantage.

For all theoretical and practical matters concerning the test, reference may be made to W. Mansfield Clark's " *The Determination of Hydrogen Ions* " (Williams and Wilkins, Co., Baltimore, 1920,

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* Søvrensen, *Biochem. Zeitschr.* for 1909, p. 13.

2nd edition, 1922). Two variations of the colourimetric method are in use, namely, that using standard buffer solutions, and the drop ratio method. The standard buffer solution method may be recommended as preferable for the present purpose, firstly, because it is generally held to be rather the more accurate of the two, and, further, because in the long run it is the quicker. When a set of buffer solutions has been made up, these will last for a long time without change if protected from the light when not in use ; and a number of determinations can, when necessary, be done at one time.

Standard Buffer Solutions.—The solutions generally used are those devised by Sørensen, the stock solutions of which are as follows :—

(1) A carefully prepared exact decinormal solution of HCl.
(2) A carbonate-free exact decinormal solution of NaOH.
(3) A tenth molecular glycocoll solution containing sodium chloride ; 7·505 grms. Glycocoll and 5·85 grms. NaCl in 1 litre.
(4) An $\frac{M}{15}$ solution of primary potassium phosphate; this contains 9·078 grms. KH_2PO_4 in 1 litre.
(5) An $\frac{M}{15}$ solution of secondary sodium phosphate, which contains 11·876 grms Na_2HPO_4, $2H_2O$ in 1 litre.
(6) A tenth molecular solution of secondary sodium citrate, made from a solution containing 21·008 grms. crystallised citric acid and 200 c.c. carbonate-free normal NaOH, diluted to 1 litre.
(7) An alkaline borate solution, made from 12·404 grms. boric acid dissolved in 100 c.c. carbonate-free normal NaOH and diluted to 1 litre.
The water used for the solutions must be boiled, CO_2-free distilled water, and the solutions must be protected against contamination by CO_2.

Mixtures of various pairs of these solutions are made in a series of test tubes of approximately uniform diameter, the final volume in each tube being 10 c.c. The exact proportions of the various mixtures will be found in Mansfield Clark's book, quoted above (1920 edition, p. 80, *et seq.*). When the various mixtures have been completed, there results a series of solutions having a range varying by small fractions from pH 1·038 to pH 13·066. To each of these tubes is added the necessary amount of the appropriate indicator (Mansfield Clark, 1920 edition, p. 40, *et seq.*) ; the tubes are then provided with well-fitting corks cut off flush with the top of the tube, the top is immersed in hot paraffin wax, and finally a small label is stuck on the tube, giving the pH figure of that particular solution. If smaller tubes are preferred, 5 c.c. instead of 10 c.c. may be made up.

Procedure.—5 c.c. or 10 c.c. (according to the size of buffer tubes used) are placed in a test tube in a rack, the amount of the appropriate indicator added, and the colour matched against those of the standard buffer tubes. In the case of coloured or turbid liquids care must be taken to place a blank tube of the sample behind the buffer tube. When constant uniformity of light is required, the colour-matching may be done in front of a daylight lamp, the effect being better if the daylight bulb is placed in a box, the front of which consists of a sheet of opal glass.

Gravimetric Estimation of Total, Suspended and Soluble Solids.

(*a*) *Total Solids.*—50 to 100 c.c. of a sewage or tank liquor and 100 to 250 c.c. or even 500 c.c. of an effluent are evaporated to dryness on the water-bath, in a small porcelain basin, the weight of which should not exceed 20 grms. (platinum is, of course, preferable), and the residue is dried in the air-bath at 100° or 105° C. until its weight becomes constant. In the case of sewages and tank liquors this is often a very tedious process, and indeed the weight sometimes goes on decreasing almost indefinitely, no doubt from the slow volatilization of certain organic compounds present. By igniting the basin with the dried residue—igniting *very* gently in the first instance—also tedious in the case of sewages and tank liquors, and again weighing, an approximation is obtained between the *Volatile* and *Non-volatile* matter present. After this first ignition it is advisable to moisten the ash with a few drops of a saturated solution of sesquicarbonate of ammonia and to re-ignite at a low temperature. If the sample is acid from the presence of fixed acid, a slight known excess of alkaline carbonate should be added before evaporation.

(*b*) *Soluble Solids.*—The same operation as has just been described is gone through, if required, with a similar quantity of the sample, filtered through a Gooch crucible.

The above process does not, of course, give all the solids, for ammonium carbonate and any other solids volatile at 100° C. are lost in the evaporation and drying. There may also be a loss of chlorine if magnesium chloride is present. Further, the ignition of the two residues, especially in the case of effluents containing nitrate, must leave the bases partly in the state of carbonate and partly as oxide. The above ignition, therefore, can only be taken as an indication whether there is anything abnormal in an effluent ; in a sewage or tank liquor it must give a fair approximation to the amount of organic matter present.

A fairly correct result, in the case of effluents, has been obtained by other workers (*e.g.*, in the Massachusetts experiments) by the addition to the liquid of a known quantity of sodium carbonate, *before* evaporation.

Solids in Suspension.

(a) *Determination of Solids in Suspension in Effluents.*

This is done by passing a given volume of the effluent through a Gooch crucible packed with asbestos.

(1) PREPARATION OF THE ASBESTOS.

The asbestos to be used should be of the quality known as Asbestos floss and should consist of silky but not too fine fibres,* which are cut down, if necessary, to lengths of about 2 c.m. A considerable quantity of this is washed with water, to remove palpable dust, and it is then digested with concentrated commercial hydrochloric acid. After another washing with water, it is redigested with small quantities of pure acid, until the latter is no longer coloured by iron. The asbestos is then thoroughly washed with water until all traces of hydrochloric acid have been removed, and preserved in the state of a rather thick pulp.

(2) PREPARATION OF THE CRUCIBLE.

The Gooch porcelain crucible employed is about 4·4 c.m. (1¾ in.) high by about 3·7 c.m. (1½ in.) in diameter at the top, and its weight should not exceed 17 to 20 grms.

The crucible is fixed into the pressure-filter flask by means of a piece of stout, wide, rubber tubing, about 2·7 to 3 c.m. internal diameter and 1·5 c.m. in length, which makes an air-tight joint when the pump is in use. Sufficient of the prepared asbestos is then put into the crucible to form a layer which will be ultimately about 0·2 c.m. deep. The pump is then turned on and the asbestos spread evenly over the bottom of the crucible, by ramming it with a glass rod flattened out at the end like a small piston rod, a gentle stream of water being run through the crucible all the time. After the asbestos has been well packed, a further quantity of 250 c.c. of water is run through the crucible in order to remove all loose particles of asbestos, and finally a few c.c. of distilled water. The crucible is then dried in the hot-air oven at 100° or 105° C. (*see* below), ignited, and weighed until the weight is constant. Two, or at most three, weighings should be sufficient to ensure that the last two weighings do not differ by more than 0·0002 grm.

(3) FILTRATION OF THE SAMPLE.

For an effluent containing, say, 3 or 4 parts suspended solids per 100,000, a convenient quantity to take for the estimation is 200 c.c. It is obvious, however, that—within reasonable limits—the volume to be taken must depend on the amount of suspended solid present. Thus, with an effluent containing 10 parts of solids, 200 c.c. would be too much, while with one containing a very small amount it would be too little.

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* In answer to enquiries, a leading asbestos firm has stated that this quality would always be obtainable, on sufficient notice being given.

In important cases it is desirable that the estimation be done in duplicate, and the mean of the two results taken.

After moistening the asbestos in the weighed crucible with a little of the sample, the pump is turned on very gently, and as much as possible of the liquid is run through under only slightly reduced pressure (a reduction of not more than 100 m.m. mercury). This precaution is very necessary if the sample carries much solid, as the latter may clog the filter if a greatly reduced pressure is used in the first instance. It is, therefore, sometimes necessary (*e.g.*, when the solids are sticky) to let the bulk of the solid settle before the filtration is begun, so that it may not enter the crucible until the greater part of the liquid is already through.

None of the sample is to be passed more than once through the asbestos. The appearance of the filtrate will at once indicate whether the packing of the asbestos has been well or badly done. The filtrate must always be examined to see that it contains no floating or deposited particles of solid. If it does, the estimation must be rejected and a new one begun.

At the end of the filtration the crucible and its contents are washed several times with small quantities of distilled water, to displace any soluble salts. The crucible is then transferred to the steam oven of temperature 100°, or to the hot-air oven, of temperature 105° C., and weighed at intervals until the weight is constant. say, to within 0·0003 gramme. After this it is ignited at a low red heat and again weighed ; this gives the *matter volatile on ignition*. Only one weighing is necessary here.

(4) PRECAUTIONS IN WEIGHING A CRUCIBLE.

It is important that a crucible should not be at a very high temperature when placed in the desiccator. While it must not be allowed to cool in the air so far as to absorb moisture, neither must it be put in so hot as materially to heat the glass of the desiccator, which would then take a long time to cool. A convenient plan is to place the ignited crucibles in the steam oven or hot-air oven, for a few minutes, so that they may take the temperature of the oven. The mass of a desiccator holding seven Gooch crucibles is about 2 kilos, while that of the crucibles is not more than about 140 grammes, hence there will be comparatively little rise in the temperature of the glass. About an hour in the desiccator will then suffice. This procedure has the further great advantage that the weighings of the prepared Gooch crucible, the crucible with suspended solid, and the crucible with ignited solid are all strictly comparable.

In the 8th Report of the Royal Commission on Sewage Disposal, Vol. II, Appendix, pp. 105–107, are to be found some details referring to points which bear on the foregoing estimation, viz. :—

In Addendum I :—

Error of the Gooch crucible estimation, when done in blank, i.e., with crucible and asbestos only.

The results of the experiments made upon this point show that :

(a) the difference between the penultimate and final weighings of the dried crucible is usually 0·0001 gramme. On 200 c.c. of effluent this would represent an error of 0·05 part suspended solid per 100,000 ;

(b) the difference in weight between the dried and the ignited crucible (containing asbestos only) is usually not more than 0·0004 gramme. On 200 c.c. of effluent this would represent a plus error of 0·2 part suspended solid and therefore of 0·2 part volatile matter per 100,000.

In Addendum II. are given a few examples of duplicate estimations of suspended solids in effluents and in sewage liquors, while Addendum III. contains a somewhat larger number of examples, not done in duplicate. In the case of effluents, the difference between the second-last and the final weighings of the dried crucible, with solids, should not exceed 0·0003 gramme. The same thing applies to sewage liquors, provided that the dried solids do not amount to more than about 0·02 gramme ; if the quantity is appreciably greater than this, the drying, and therefore the weighing, becomes unsatisfactory. Addendum IV shows the effect of settlement, for 1 and 2 hours respectively, upon a number of typical effluents.

(b) *Determination of Solids in Suspension in Sewages and Tank Liquors.*

This is done in exactly the same way as has just been described, excepting that much less of the sample is required in this case. Twenty-five c.c. of an average sewage and 50 c.c. of an average tank liquor are convenient quantities to take. But here, again, no hard-and-fast rule can be laid down, since the above liquors vary greatly in strength and in suspended solid content.

Twenty-five c.c. may appear to be a very small quantity to take of an average sewage (containing, say, 30 parts suspended solids per 100,000), but any disadvantage in this respect, as compared with taking a larger volume, is counter-balanced by the lesser time required to filter the liquor and to dry the Gooch crucible after the filtration, and the consequent lesser risk of loss in weight from the slow distillation of some of the organic solids present. This conclusion is based on G. T. P. Tatham's work.

COLLOIDAL MATTER.

In the foregoing section nothing has been said about the solids which are always present in the colloidal state in sewages and tank liquors, and also to a lesser degree in effluents. The Gooch filtrates from ordinary crude sewage and septic tank liquor appear to contain something like 3 to 5 parts of colloidal matter per 100,000. Good land effluents may be regarded as free from colloidal matter, and bright sparkling effluents from artificial filters as practically free also. Effluents from contact beds and from percolation filters, however,

which show distinct opalescence, contain more or less colloidal matter.

There can be little doubt that the colloidal matter of a sewage liquor or effluent discharging into a stream must usually travel a long distance in the colloidal state. Therefore, so far as natural purification by the stream is concerned, it must come more into the category of matter in solution than of matter in suspension.

Excepting perhaps in the case of very highly colloidal sewage liquors, the determination of suspended solids by the Gooch crucible method, as just described, does practically discriminate between the matter in suspension and the colloidal matter plus matter in solution with which the stream has to deal. No doubt, however, in the case of sewages and tank liquors, at all events, the asbestos pad of the Gooch crucible does retain some of the colloids along with the suspended solids proper.

What is really wanted, therefore, for the further elucidation of the subject, is a good and quick direct method for estimating the colloidal, as apart from the true suspended, matter of a sewage liquor or effluent. In view of the comparatively scanty data available, it seems doubtful whether some estimates of the amount of colloidal matter present in sewage liquors may not have been somewhat exaggerated.

The Centrifuge method for determination of Suspended Solids.

As there is a considerable body of opinion in favour of the centrifuge method for determining suspended solids, and as in the view of most users it is simpler and involves less trouble than the Gooch crucible process, it is submitted as an alternative method for routine use. For cases which may involve dispute, however, the Gooch crucible should be used.

Procedure.—The method of carrying out the test varies but little in different laboratories. About 20 c.c. of sewage, 50 c.c. of tank liquor, or 100 to 200 c.c. of effluent are centrifuged till the solids settle out ; the upper liquid is then poured off, the residue rotated again with distilled water, and the second residue washed with as little water as possible into a weighed porcelain crucible. After this water has been evaporated off, the crucible and contents are dried at 100° or 105°, weighed till the weight remains constant, ignited and re-weighed.

In cases where the suspended matter is very low, a larger volume of the sample is allowed adequate settlement, the top water siphoned off, and only the lower layer centrifuged.

This method records only particulate matters, whereas it is possible that the Gooch crucible may also retain some colloids.

Estimation of Dissolved Oxygen and of Dissolved Oxygen Absorption. Winkler's method* as modified by Rideal and Stewart.†

The principle on which this test depends is the oxidation in an alkaline liquid of manganous oxide to a higher oxide of manganese, the subsequent liberation of iodine from potassic iodide by this in the now acidified solution, and the titration of the liberated iodine by thiosulphate.

For the 5 *days' test at* 18·3° C. the dilution required by an average effluent is 1 volume effluent + 4 volumes good tap water. Should the effluent be of poor quality, it would be necessary to take, say, 9 volumes of water.‡ For tank liquors the dilutions would usually be with 49 and 99 volumes of tap water. In every case the dilution should be stated.

For the 48 *hours' test*, 1 volume of effluent + 2 volumes tap water.

It is advisable not to use up more than 50 per cent. of the oxygen present ; on the other hand, if the dilution be too great, the action will be somewhat retarded.

This test involves the use of a cold water incubator, of temperature 18·3°C. (65F°.)

The tap water with which the dilutions are made should be kept over-night in a Winchester quart bottle, two-thirds full, at about 18° or 19° C., and the bottle should be well shaken up some little time before the determinations are made (not immediately before, as in that case the small air bubbles would not have time to escape). This ensures the water not being super-saturated at that temperature. The question of the nature of the water to be used for dilution has been a good deal discussed. Further work on this would be desirable.

Control determinations with the tap water alone should be done, to make sure that the water itself does not take up any appreciable quantity of oxygen.

The solutions required are :—

  (1) Concentrated Sulphuric Acid.

  (2) $\frac{N}{8}$ Potassium Permanganate (3·94 grm. per litre).

  (3) Potassium Oxalate (2 per cent. of the crystallized salt).

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* *Berichte*, Vol. XXI, p. 2843 (1888).

† *Analyst*, Vol. XXVI, p. 141 (1901).

‡ The diluting water must be free from copper or lead. From a few experiments made by E. Ardern and E. Halliwell, respectively, it would appear that copper begins to exert an inhibiting action on the absorption of dissolved oxygen at a concentration below 0·125 part Cu per 100,000, and lead at a concentration of about 0·01 per 100,000. It would be desirable to have further experiments made, in order to determine the limiting figures for both copper and lead. It should be borne in mind, in this connection, that the nature of the water (hard or soft, etc.) might possibly exert an influence here.

(4) Manganous Chloride (33 per cent. of $MnCl_2$).

(5) A mixed solution of caustic potash and iodide of potassium containing 70 per cent. KOH and 10 per cent. KI.

(6) Concentrated Hydrochloric Acid (*free from chlorine*).

(7) Approximately $\frac{N}{20}$ Sodium Thiosulphate solution (*i.e.* containing about 12 grms. of the salt and 2 grms. of sodium carbonate).

Bottles of 340 to 360 c.c., provided with well-fitting stoppers, are used for the test, the volume of each bottle being marked on it. If any difficulty arises with small bubbles of air, when a bottle is being closed, the lower part of the stopper may be rounded by grinding.

After a dilution has been made in a flask of ample size, and the contents of the flask have been gently mixed, the two bottles required for one determination are filled quietly, and so far as possible in a similar manner, with the diluted effluent, a little of the mixture being allowed to overflow, in case of the top layer having become slightly more oxygenated than the rest in the act of filling. Both bottles are then stoppered, being completely full of liquid. One bottle (B) is placed in the incubator for 48 hours, or 5 days, while in the other (A) the oxygen in solution is at once determined, as follows :—

0·9 c.c. sulphuric acid are dropped in, and then sufficient of the permanganate solution to leave a slight excess of the latter after the whole has been mixed and has stood for 20 minutes (stoppered, of course) ; 1 to 2 c.c. of the permanganate are nearly always sufficient for this. The main object of the permanganate addition is to oxidize any nitrite present to nitrate.

After 20 minutes have elapsed, the excess of permanganate is destroyed by the addition of about 1 c.c. of the oxalate solution, the bottle being at once re-stoppered and its contents mixed.

When the liquid has become colourless*, the stopper is again removed, and 1 c.c. of the manganese chloride is run in from a pipette at the bottom of the bottle, the pipette being dried outside with a fragment of filter paper before insertion and closed with the finger when withdrawn ; and, immediately afterwards, 4 c.c. of the mixed (KOH+KI) solution are added ; in this latter case, the point of the pipette need only be a little below the surface of the liquid. The fine point of this pipette should be cut off, so that the pipette may empty quickly.

The stopper having been again inserted, the bottle is turned over once or twice, to mix the contents, and after a few minutes turned over again and allowed to stand for a further few minutes. The second rotation (after a short interval from the first) ensures good settlement of the hydroxides of manganese.

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* In the case of poor effluents and tank liquors, a brown precipitate may form, and this must be given time to disappear.

5 c.c. of hydrochloric acid are now run in from a pipette, and the bottle is re-stoppered and kept in the shade for 5 minutes, or so, with occasional rotation. 20 c.c. of the liquid are now pipetted out of the bottle and rejected, and the remainder is titrated with thio-sulphate, using some *clear freshly-made* starch solution towards the end of the titration. The life of a solution of starch may be lengthened by the addition of a few drops of chloroform, but this somewhat impairs its delicacy.

For practical purposes, no correction need be made for the 8 c.c. or so of added reagents (the hydrochloric acid hardly counts here). This no doubt contains less oxygen in solution than 8 c.c. of fully saturated water, but as to how much less no data are available. Assuming that the capacity of the bottle is 350 c.c., the oxygen found may be taken as derived from 350—20=330 c.c. of the diluted effluent.

At the end of 5 days (or whatever other period of time) the oxygen remaining in solution in bottle (B) is determined in the same way. The difference between the two determinations represents the oxygen taken up by the effluent in the interval.

The dissolved oxygen is calculated as follows :—

If N=number of c.c. of Thio. used.

S=strength of Thio., expressed in grms. of oxygen per c.c.

V=volume of the bottle in c.c.

Then, dissolved oxygen, in parts per 100,000 $= \dfrac{100,000 \times N.S.}{V}$

To give a concrete instance :—

An effluent was incubated with four volumes of tap water.

Dissolved oxygen in mixture at start :—

Vol. of bottle 341–20   =321 c.c.

Thio. used   = 6·95 c.c.

Strength of Thio.   = 0·0003773 grm. oxygen per c.c.

Hence, dissolved oxygen $= \dfrac{0·0003773 \times 6·95 \times 100,000}{321} = 0·817$ (a)

Dissolved oxygen in mixture at end of period of incubation :—

Vol. of bottle 338–20   =318 c.c.

Thio. used   =4·11 c.c.

Similarly, dissolved oxygen=0·488 (b)

Subtracting (b) from (a) we have :—

Dissolved oxygen taken up by 100,000 parts of the *mixture* =0·329 grm.

As the mixture was only one-fifth effluent it is necessary to multiply this figure by 5, in order to get the absorption by one hundred thousand parts of effluent, *i.e.*, 1·65 grms.

A. F. Girvan, when working for the Royal Commission on Sewage Disposal, devised a box of moderate dimensions which allows of the Winkler method being used in field work. It contains

the necessary bottles for water and for reagents, together with a short burette, pipettes, etc.

The Five Days Dissolved Oxygen Absorption test, in its various bearings, is discussed at length in the 8th Report of the Royal Commission on Sewage Disposal, Vol. II, Appendix, pp. 62-84, and p. 93 *et seq.* The recommendation by the Royal Commission of this, as a standard test, was arrived at by working back from the water of the stream to the sewage liquor or effluent discharging into it, making certain observed conditions of the stream itself the basis of any standard or standards to be suggested. Prolonged observations on streams led to the conclusion that the 5 days' test (taken along with the determination of suspended solids) afforded a better criterion of the polluting character of a sewage liquor or effluent than any of the other tests commonly employed.

The most delicate chemical index of *recent* sewage pollution is the increase in the figure for ammoniacal nitrogen yielded by the water of a stream shortly below the outfall, as compared with the water above it. Decrease in oxidizable matter and decrease in ammonia go on concurrently as a polluted water finds its way down stream. Still, the observations above referred to, taken as a whole, showed that the determination of ammoniacal nitrogen is less to be relied on as indicating the polluting, *i.e.*, de-oxidizing, power of an effluent than the 5 days' test ; and the same applies to the incubator test and to the determination of albuminoid nitrogen and of oxygen absorbed from permanganate, valuable as those are.

With regard to sewage effluents passing into drinking water streams, it must not be forgotten that good effluents (such as those passing the chemical standards recommended by the Royal Commission on Sewage Disposal) are still very impure bacteriologically, unless sterilized. Wherever, therefore, any possibility exists of the recipient of a chemical analysis being ignorant of this fact, a suitable note of warning should be added. In cases where drinking water is chlorinated, very minute traces of phenoloid bodies, if present in the water, are liable to give rise to unpleasant tastes ; the importance of tests for such bodies in purified sewage effluents has, therefore, to be borne in mind in those cases.

The reason for selecting the temperature of 18·3° C. (65°F.) for the test was because it is unusual in this country for the water of even a sluggish river in any non-manufacturing district ever to exceed it. Of course, in manufacturing areas, where the same water is used over and over again, its temperature may rise much higher.

The main objection which has been taken by some to this test is that it requires 5 days for completion. In the work done for the Royal Commission on Sewage Disposal the 48 Hours' test was also largely employed, but it was felt that for purposes of a standard the 5 Days' test was less liable to error.

E. Halliwell has recently suggested that a 3 days' test at 26·7°C. might be substituted for the 5 days' test at 18·3°C., and the table

of results given in Appendix No. 5 shews that effluents obtained by various methods of treatment, and of different degrees of purity, give similar figures by the two tests. R. Eaton (Appendix No. 5) found similar concordance in a number of effluents from a particular works. Whilst the balance of opinion is still in favour of the 5 days' procedure, the test at the higher temperature for the shorter period may be employed if it is desired to obtain quicker results or if the completion of the 5 days' test falls on a non-working day. In cases, however, which may involve dispute, it is recommended that the 5 days' test be employed.

There is also a good deal to be said for a 24 hours' test as a measure of purification, the effluent being warmed up to 18·3°C. in the first instance and well oxygenated by shaking up with air. Further, E. H. Richards*has pointed out that the ratio of the 24 hours' to the 5 days' test may be applied to a polluted water of unknown origin, with a view to ascertaining whether it has been polluted by a sewage or tank liquor, on the one hand, or by a fairly well purified effluent, on the other ; in the former case the ratio would be higher than in the latter. The 24 hours' and 5 days' tests, taken together, might give a better indication of the quality of an effluent than the 5 days' test alone.

For a comprehensive study of the subject of Dissolved Oxygen Absorption, see Theriault, *U.S. Public Health Service, Public Health Bulletin, No. 173 (1927)*, where the work done in the various different countries is reviewed.

John T. Thomson advocates the saturation of an effluent with oxygen instead of with air and then the measurement of the dissolved oxygen absorption in 24 hours at 18·3°C. (*Proceedings of the Association of Sewage Works Managers for 1925, p. 59*).

Of further recent work on the absorption of dissolved oxygen by effluents, mention may be made of the following :—

" The Effect of Chlorine on the Dissolved Oxygen Absorption Test." (Gaunt and Abbott, *Journ. Soc. Chem. Ind.*, Vol. 45, No. 37, pp. 323–324 T).

" The Dissolved Oxygen Absorption Time Relation of Activated Sludge Effluents " (Gaunt and Abbott, *Ibid.* Vol. 47, No. 2, pp. 14–16 T.).

" Studies on the Dissolved Oxygen Absorption Test." (Cooper and Read, *Ibid.*, Vol. 46, No. 16, pp. 154–156 T ; Vol. 46, No. 42, pp. 413–414 T ; Cooper and Nicholas, *Ibid.*, Vol. 47, No. 44, pp. 320–322 T).

In these two last the effect of various substances on the absorption of dissolved oxygen by sewage effluents is described, the substances employed being (*a*) phosphates and metallic salts ; (*b*) plant stimulants ; and (*c*) catalysts in chemical processes.

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* *Royal Commission on Sewage Disposal*, 8th Report, Vol. II, Appendix, p. 84.

The Miller Method for the Determination of Dissolved Oxygen*

The method as set out by Miller is as follows :—

"To 50 c.c. of the water contained in a 100 c.c. Nessler glass are added 5 c.c. of alkaline tartrate such as is used for Fehling's solution, and one drop of pheno-safranine solution (1 grm. in 2,000 c.c. of water) ; then, from a 10 c.c. graduated pipette, a solution of ferrous sulphate (·22 grm. of pure $FeSO_4$ and 1 c.c. of concentrated H_2SO_4 in 100 c.c.) is run in just below the surface of the liquid, stirring gently with the pipette until the colour is discharged, looking through the cylinder horizontally. The ferrous sulphate is added 1 c.c. at a time until the colour begins to fade, then in quantities of ·5 c.c. to the end. There is a slight colouration at the surface of the liquid, but if the stirring is not too vigorous this does not interfere. The outlet hole of the pipette should not be more than 1 m.m. in diameter, to minimise diffusion."

"The pipette reading gives the cubic centimetres of oxygen per litre. Theoretically, 1 c.c. of ferrous sulphate of the above strength does not equal 1 c.c. of oxygen per litre, working on 50 c.c. of sample (0·25 per cent. $FeSO_4$ is the theoretical strength); but under the conditions stated I have found that the above strength gives correct results."

"Each experimenter should standardize his ferrous sulphate against water of known oxygen content, say, distilled water shaken with air until saturated, taking the temperature and referring to Roscoe and Lunt's table (Sutton's *Volumetric Analysis*, 6th Edition, p. 260) for the amount of dissolved oxygen present."

The above method is a quick one and is suitable for field or laboratory use in the hands of trained persons.

The following modification of this test increases its accuracy.† About 3 c.c. of purified paraffin oil are gently distributed on to the surface of 50 c.c. of the water contained in a 100 c.c. Nessler or similar glass, provided with a glass stirring rod suitably twisted at its lower end. 5 c.c. of the alkaline tartrate and one drop of the pheno-safranine solution are in turn introduced below the paraffin layer and the contents are quietly mixed without breaking the surface ; then, from a burette, sufficiently elongated to pass below the paraffin, the solution of ferrous sulphate is run in (1 c.c. at a time, and finally 0·5 and 0·25 c.c.), gently stirring with an up-and-down movement of the rod, until the colour is discharged. The end of the reaction is thus sharply defined, the exclusion of air in this manner

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* *Journ. Soc. Chem. Ind.*, 1914, No. 4, Vol. 33, p. 185.

† *Provincial Board of Health of Ontario, Bulletin No. 7.* "Sewage and Water." Recommended methods for physical and chemical examination, including Interpretation of Water Analysis. *Division of Sanitary Engineering.* Revised Edition (1920).

providing against surface discolourization. Consecutive titrations should agree to within 0·1 c.c.

The appended table by Ardern (Appendix No. 6, p. 70), giving comparative figures for dissolved oxygen and dissolved oxygen absorption in different types of effluent by the Winkler and the modified Miller methods, respectively, shows very good agreement in the two cases. It may be added, speaking generally, that when the samples tested contain a fair amount of dissolved oxygen the results are quite satisfactory, but difficulty arises when only a little ferrous salt has to be added to obtain the end point. As the tartrate solution is a strong one, it does not mix readily with the sample under examination, and very little stirring is permissible, otherwise atmospheric oxygen is absorbed. Thus, when only 0·5 c.c. or less of the iron solution has to be added, the mixture cannot be satisfactorily stirred by the time the end point is reached ; on the other hand, with 1 c.c. or more of the iron solution there is little trouble and good results are obtained. In other words, the percentage error tends to increase as the dissolved oxygen content decreases. To conclude—when used as a field test, or for sewage effluents (undiluted, before and after 24 hours' incubation at 18·3°C.), so long as a fair amount of oxygen is present in solution, the test is applicable, but it cannot replace the Winkler method for accuracy. For cases which may involve dispute, therefore, the Winkler method is recommended.

Mohr's Method (modified) for the Determination of Dissolved Oxygen.

A further reliable method for the estimation of dissolved oxygen is that of Mohr,[1] as modified by Letts and Blake.[2] It is based on the oxidation of a ferrous salt. (*Cf.* also Soper, *Metropolitan Sewerage Commission of New York*, 1912 Report, p. 229 *et seq.*).

Determination of the " Strength " of Sewage.

See Adeney's fundamental work on the subject, published in the *Trans. Royal Dublin Society* and in the *Proc. Royal Irish Academy*, from 1891, onwards ; *Royal Commission on Sewage Disposal*, 5th Report, Appendix VI, pp. 5–109 ; also his recently published volume " The Principles and Practice of the Dilution Method of Sewage Disposal " (Cambridge University Press, 1928).

Accurate gauging is of the first importance when samples of a sewage have to be taken, in order to determine its strength.

The " strength " of sewage is measured in terms of the oxygen required to oxidize its organic matter and ammonia bio-chemically— 100,000 parts of a sewage of average strength require about 100

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[1] *Lehrbuch der Titrirmethoden*, 4te Auflage, p. 239 (1874).

[2] Letts and Blake, *Sci. Proc. Royal Dublin Soc.*, Vol. 9 (N.S.), Part 4, No. 33, p. 454 (1901).

Letts, *Royal Commission on Sewage Disposal*, 5th Report, Appendix VI, p. 221 *et seq.* (1908).

parts by weight of oxygen for this purpose.*   The bacterial treatment of domestic sewage is now so well systematized that the volume which can be dealt with on unit of filter depends on the strength of the sewage or tank liquor to be treated.†

To estimate the strength of a sewage or other polluting organic liquor, a small measured volume is mixed with a large measured volume of good tap water, *i.e.*, with excess of dissolved oxygen, and the oxygen in solution is determined (*a*) at the time of mixing and (*b*) after all the oxidizable matter present has been oxidized.   The difference between the two figures found gives the amount of oxygen taken up by the sewage or other liquor.

The procedure followed in this determination of dissolved oxygen absorption is to be found in the Eighth Report of the Royal Commission, Vol. II, Appendix, p. 93 *et seq*. [Cd. 6943 (1913)], but an outline of it may be given here.   The requisite dilution having been made with good tap water at a temperature of about 18° C, the liquid is poured quietly, in alternate sections, into three bottles, (*a*) a small one of about 350 c.c. capacity, in which the determination of the initial oxygen is immediately made, and (*b*) two duplicate quarter-Winchesters each of 600–700 c.c. capacity, with well-fitting stoppers. These bottles should be tested carefully beforehand, to make sure that the stoppers are really tight-fitting.   The bottles are of course filled full to overflowing.   After the stopper of a quarter-Winchester has been firmly inserted and tied down with tape, a small piece of wide rubber tubing of about 20 mm. internal diameter and 50 mm. long is slipped over it, the top of the rubber remaining about 15 mm. above the head of the stopper.   The rubber joint is then nearly filled with mercury and the bottle set aside until the oxidation has completed itself.   Unless the glass stopper should have been a bad fit, which rarely happens, this forms a satisfactory joint for the purpose.

At the end of the period allowed for this " long aeration," say, two or three months at laboratory temperature, the small quantity of gas which has collected at the top of the bottle is transferred and analysed, the figure for the oxygen which it contains being added to that for the oxygen in the residual liquid.

This transference, which may be rather troublesome, is best done as follows :—

The mercury of the joint is poured off, the rubber tube carefully removed, and the tape binding the stopper cut, the bottle being held slanted, so that the gas bubble may lodge in the shoulder.   The stopper is now almost invariably very firmly fixed (there being a slight vacuum in the bottle), and it does not always yield to tapping. In that case a few drops of water should be poured on the top of the

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* McGowan, 5th Report Royal Commission on Sewage Disposal, App. IV, pp. 1–9. (1910) (Cd. 4282) ; *Journ. Soc. Chem. Ind.*, Vol. XL, No. 12, pp. 148–150T.

† McGowan and Frye, 5th Report Royal Commission on Sewage Disposal, App. IV, pp. 52–72 (Cd. 4282).

neck at the stopper, or the bottle should be inverted, with its neck in water for a few minutes. After taking out and drying, the stopper will now in all probability be amenable to tapping, though sometimes the aid of a *Bunsen* burner is required. All this time (of tapping, &c.) the bottle must have been held slanting ; further, when the stopper is being tried, to see whether it has become loosened, this has to be done very carefully, otherwise a little air may be sucked into the bottle (as is seen by the tiny bubbles rising through the water in the neck). The bottle is then inverted over mercury in a trough, the stopper removed, and the gases drawn into a suitable mercury gas-holder. For the transference from the quarter-Winchester, a narrow tube of " gum elastic," about 2·5 mm. internal diameter and 33 to 35 cm. (13 ins. to 14 ins.) long, fixed into a wider rubber tube connecting with the small gas-holder, is most convenient. The former is of the small diameter required, and is sufficiently rigid (without being too much so) to remain steady in the inverted bottle.

Again, in making the estimation of the oxygen remaining in the water of the quarter-Winchester from which the gases have just been carefully removed, the bottle now contains a little mercury (which has filled up the slight vacuum and which has also replaced the small quantity of water unavoidably transferred along with the gases). This mercury has no action upon any of the reagents used in the oxygen determination, until the stage of liberating iodine is reached. Immediately the iodine has been liberated, however, and the solution made uniform by one or two rotations, the greater portion of the liquid is poured off, for titration, into a smaller bottle of known capacity (say 350 c.c.), or into two smaller bottles of about 300 c.c. and 250 c.c.; *i.e.*, the iodine-containing water and mercury are not allowed to remain in contact. If they are, the estimation is spoilt. The few seconds of time that the two layers are in contact in the quarter-Winchester introduces no appreciable error. Or, instead of liberating the iodine in the water in the presence of some mercury and immediately pouring off, an alternative method is to siphon the liquid into a smaller bottle, previously filled with carbon dioxide, rejecting the first and last portions.

What has just been said applies also, of course, to any " long aeration "—whether of mud, sewage liquor, trade waste or effluent, &c.

NOTE.—It is advisable, before risking the contents of a bottle which has been standing jointed for at least two months, to disjoint a " dummy " quarter-Winchester, full of water excepting for one or two c.c. of air. This ensures mastery of the technique of the gas transference, the subsequent liberation of iodine in the liquid, and the rapid decantation of the latter from the mercury.

ANALYSIS OF THE TRANSFERRED GASES

These consist of nitrogen and oxygen, with a trace of carbon dioxide. Their total volume is but small—usually not more than a few c.c., hence it is essential that only small quantities of absorbents

should be used in their analysis. The apparatus devised by Adeney *, both for boiling out gases from waters and then analyzing them (or gases from septic tanks, filter beds, &c.), is very convenient, especially if modified as described in the 4th Report, Royal Commission on Sewage Disposal, Vol. IV, Part V, p. 52, to which the reader is referred.

Approximate Method for Determining " Strength."†

In cases where time does not allow of a determination of the strength of sewage liquors by the foregoing " long aeration " method, a good approximation can be arrived at for domestic sewage‡ by estimating the ammonical and albuminoid or organic nitrogen and the " oxygen absorbed " from $\frac{N}{8}$ permanganate in 4 hours at 27° C. and then applying the following formula to the figures so obtained :—

For Sewages :—(Ammon. + Organic N) × 4·5 + (Ox. abs. in 4 hours × 6·5§).

For Septic Tank Liquors :—(Ammon. + Organic N) × 4·5 + (Ox. abs. in 4 hours × 6·5§).

For Precipitation Liquors :—(Ammon. + Organic N) × 4·5 + (Ox. abs. in 4 hours × 6·0§).

The subject is dealt with in detail in the 5th Report of the Royal Commission on Sewage Disposal, Appendix IV, p. 1, *et seq.* (1910), (Cd. 4282), to which the reader is referred.

Determination of " Strength " by Oxidization with Potassic Bichromate and Sulphuric Acid.

W. E. Adeney and Miss B. B. Dawson have recently studied the action of acid bichromate upon various organic compounds and upon sewage, with a view to its application for arriving quickly at the total oxidizability of sewage and other polluting liquors (*Proc. Royal Dublin Soc.*, Vol. XVIII (N.S.), pp. 199–202 (1926). The end products of this oxidation are taken as carbon dioxide, water and ammonia. The analytical procedure is fully set out in the paper just mentioned and also in Adeney's book : " *The Dilution Method of Sewage Disposal*," p. 130 *et seq.*

It would be very desirable to have a considerable number of comparative estimations of oxidizability of sewage liquors made :—

(*a*) by the " long aeration " method (taking this as the standard);

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* *Trans. Royal Dublin Society*, Vol. V (Series II), p. 39, *et seq.*

† *Cf.* McGowan, 5th Report Royal Commission on Sewage Disposal, App. IV, pp. 1–9. (Cd. 4282.)

‡ Apart from cases where large volumes of trade wastes, containing *e.g.* starch, glucose, or gas liquor, are present.

§ Note.—When N/80 permanganate has been used in the " oxygen absorbed " test, this figure would have to be further multiplied by 1·6, in order to give an approximately correct result.

(*b*) by the acid bichromate method ;

(*c*) by the approximate method (ammonia and permanganate) and application of the formula given above.

An estimation with acid bichromate requires only a day or two for completion, and it is to be expected that the method will prove of great value for arriving rapidly at the " strength " of a sewage.

Sludges.

The analysis of sludges calls for no special remarks, the various tests being simple and straightforward. The tests generally made are those for moisture, alkalinity, organic nitrogen, grease, and mineral and organic matters. Other tests may be added in special cases if found necessary. Two points should be borne in mind in the case of sludges containing grease. The first is that the sludge should be dried at a temperature of 100° C., as certain sludge greases are apt to burn slightly if dried at a higher temperature. The second point is that when it is proposed to determine the grease in a sludge, the latter should be acidified with hydrochloric acid before drying.

Moisture.—10 grms. of the sample are dried at 100° C. until the weight is constant. The loss of weight is recorded as percentage of moisture.

Alkalinity or Acidity.—This is best ascertained by diluting 5 grms. of the sludge with a relatively large volume of distilled water, and determining in the usual way.

Grease.—A weighed quantity of the acidified dry sludge is thoroughly extracted in a Soxhlet apparatus, using petroleum ether as the solvent. After distilling off most of the solvent the residue in the flask is placed in the oven at 100° C. for one hour, cooled and weighed, the grease being expressed as percentage on the dry solids.

An alternative method for routine purposes is given in Appendix 7, p. 71.

Organic Nitrogen.—The organic nitrogen should be determined by the Kjeldahl method, using potassium or sodium sulphate to aid in the digestion.

One grm. of the dried sludge is digested with 20 c.c. of sulphuric acid in a Kjeldahl flask, a few grammes of potassium or sodium sulphate being also added. When digestion is complete, the after procedure is the same as that in the case of sewages, the ammonia being distilled over into decinormal sulphuric acid. The result is expressed as percentage of nitrogen on the dry solids.

Mineral and Organic Matters.—Although, to be strictly accurate, those should be termed fixed and volatile matters, the term mineral and organic matter is generally adopted in this country and is quite sufficiently true in this connexion.

A weighed quantity of the dried sludge is first heated gently, and afterwards strongly ignited until all traces of carbon have been burnt off. After cooling and weighing, the residue is expressed as percentage of mineral matter, the loss in weight being expressed as percentage of organic matter.

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APPENDIX 1.

Changes undergone by Sewage when kept in a full bottle (not in the dark).

On Monday, 9th June, 1902, at 11 a.m., three Winchesters of Ealing Sewage were drawn. At 5 p.m. in the laboratory their contents were poured into a large pail, and any large pieces of paper and other coarse solids were rejected. The pail was then kept constantly stirred, and four half Winchesters were filled from it by pouring into each a beakerful in turn, *i.e.*, every bottle received one beaker before the second beakerful was poured into any. So far as could be judged, the samples were very even. The bottles were filled completely and kept at laboratory temperature.

	No. 1.	No. 2.	No. 3.	No. 4.
Analysed ..	10th June, 1902	11th June, 1902.	12th June, 1902.	16th June, 1902.
Parts per 100,000 *by weight.*				
Ammoniacal nitrogen	9·98	10·21 ⎱ Two drops of	10·68 ⎱ Two drops of	11·78 ⎱ Six drops of
Albuminoid nitrogen	1·82	1·79 ⎰ Na₂ CO₃ Aq. added.†	1·54 ⎰ Na₂ CO₃ Aq. added.	0·72 ⎰ Na₂ CO₃ Aq. added.
Nitrous nitrogen ..	0·0	——	——	——
Nitric nitrogen ..	* Not tested for.	——	——	——
Total nitrogen by Kjeldahl method	13·56	13·48	13·49	13·57
Blank	(0·33 in 10·19)	(0·33 in 10·13)	(0·33 in 10·14)	(0·33 in 10·20)
" X " nitrogen ..	1·76	1·48	1·27	1·07
Total Organic nitrogen ..	3·58	3·27	2·81	1·79
"Oxygen absorbed" from N/8 permanganate at 26·7° C. (80° F.) *at once* ..	3·00	3·39	3·93	5·10
"Oxygen absorbed" from N/8 permanganate at 26·7° C. (80° F.) *after 4 hours* ..	16·87	15·77	15·23	14·53
Chlorine	10·60	10·60	10·54	(a) (b)‡ (c) 10·66 10·50 10·30
Total solids (gravimetrically) ..	119·7 ⎰ 56·4 Volatile ⎱ 63·3 Non-Vol.	115·7 ⎰ 53·6 Volatile ⎱ 62·1 Non-Vol.	114·1 ⎰ 53·4 Volatile ⎱ 60·7 Non-Vol.	112·3 ⎰ 55·8 Volatile. ⎱ 56·5 Non-Vol.
Solids in suspension	42·1 ⎰ 28·9 Vol. ⎱ 13·2 Non-Vol.	40·3 ⎰ 30·2 Vol. ⎱ 10·1 Non-Vol.	40·2 ⎰ 34·1 Vol. ⎱ 6·1 Non-Vol.	36·9 ⎰ 29·4 Vol. ⎱ 7·5 Non-Vol.
Solids in solution ..	77·6 ⎰ 27·5 Vol. ⎱ 50·1 Non-Vol.	75·4 ⎰ 23·4 Vol. ⎱ 52·0 Non-Vol.	73·9 ⎰ 19·3 Vol. ⎱ 54·6 Non-Vol.	75·4 ⎰ 26·4 Vol. ⎱ 49·0 Non-Vol.
Parts per 100,000 *by Volume.*				
Solids by centrifuge	289	244	257	199
Remarks	Turbid and brown. Not a very large amount of brown sediment. Sewage smell. Alkaline.	The same in character as Sample No. 1	Much the same as Nos. 1 and 2.	Rather more turbid than the preceding samples. There was now a smell of sulphuretted hydrogen along with that of sewage. Not appreciably blackened. Alkaline.

* Though in all probability no nitrate was present, it might have been well to have tested for it in the first instance.

† This solution was about half normal, *i.e.*, contained about 27 grms. Na₂CO₃ per litre.

‡ Estimations (a) and (b) were done by filtration and evaporation only ; in the case of (c) a little sodium carbonate was added before evaporating, and the residue was charred, etc.

APPENDIX 1—*continued*.

During the week covered by the foregoing estimations the temperature was very low for the season. On Tuesday, 10th June, the temperature of the sewage itself in the bottle was 16°–18° C. (61°–64° F.), and this would probably be about the average temperature throughout.

The main conclusions to be drawn from this experiment are;—

1. That sewage, in the absence of oxygen and nitrate, undergoes little change for the first two days at a moderate temperature, and for six days, at all events, there is no alteration in the total amount of nitrogen present.

2. The changes which it does undergo are in the following direction :—

(*a*) The ammoniacal nitrogen increases slowly at the expense of the organic nitrogen, there being a steady diminution *both* in the "albuminoid" and in the "X" nitrogen.

(*b*) There is a gradual increase in the amount of readily putrescible matter as measured by the "oxygen absorbed" from permanganate *at once*.

(*c*) The suspended solids also show a slight diminution in quantity, but upon this point it is not safe to generalise without further data.

APPENDIX 2.

Experiments showing the breaking-down effect of Water and of Alkali upon Sewage.

(a) *Dilute Solution of Caustic Soda.*

10th November, 1898.—To 100 c.c. of sewage, 50 c.c. distilled water and 0·05 grm. of caustic soda were added, and the liquid was then distilled. Subsequently five other separate quantities of 50 c.c. water were added and the distillation was repeated after each addition, but ammonia still continued to be given off. *This proves that it is inadmissible to add to a sewage more than the slightest excess of alkali.*

(b) *Freshly-precipitated Silver Oxide.*

This was taken as being a mild " alkali."

1898. Nov. 14th	70 c.c. Sewage, about 50 c.c. distilled water, and 0·2 grm. moist oxide of silver were taken :		Found :
,, ,,	Distilled 50 c.c. ..		Too much ammonia to nesslerize.
,, 15th	Added 50 c.c. water and distilled ..	{ 1st 25 c.c.	Nessler ; very dark brown
		2nd 25 c.c.	,, ,, ,,
,, ,,	Added 50 c.c. water and distilled ..	{ 1st 25 c.c.	,, ,, ,,
		2nd 25 c.c.	0·000019 grm. NH_3.
,, ,,	Added 50 c.c. water and distilled ..	{ 1st 25 c.c.	·000015 (Pale yellow)
		2nd 25 c.c.	·000002 (trace)
,, 16th	Added 50 c.c. water and distilled ..	{ 1st 25 c.c.	·000022
		2nd 25 c.c.	·000009
,, ,,	Added 50 c.c. water and distilled	{ 1st 25 c.c.	·000009
		2nd 25 c.c.	·000010
		3rd 25 c.c.	·000009
,, 17th	Added 50 c.c. water and distilled	{ 1st 25 c.c.	·000015
		2nd 25 c.c.	·000010

Moist oxide of silver thus breaks down sewage much less energetically than dilute caustic soda, but still its action is very marked.

APPENDIX 2—*continued.*

(c) *Water alone.*

1898 Nov. 10th	100 c.c. of sewage were mixed with 75 c.c. distilled water, and 75 c.c. of the mixture were distilled over. Then six further additions of water were made, as given below, 50 c.c. at a time :—		
		Distillate.	NH$_3$ found.
,, ,,	100 c.c. sewage + 75 c.c. water	1st 75 c.c. ..	Too much to estimate
,, ,,	50 c.c. water added..	2nd 50 c.c. ..	,, ,,
,, ,,	50 c.c. ,, ,, ..	3rd 50 { 25 c.c. .. { 25 c.c. ..	,, ,, 0·0001 grm. (*i.e.*, ·01 part per 100,000).
,, 11th	50 c.c. ,, ,, ..	50 { 1st 25 c.c. { 2nd 25 c.c.	·000019 grm. ·000010
,, ,,	50 c.c. ,, ,, ..	50 { 1st 25 c.c. { 2nd 25 c.c.	·000007 none
,, 12th	50 c.c. ,, ,, ..	50 { 1st 25 c.c. { 2nd 25 c.c.	·000008 ·000003
,, ,,	50 c.c. ,, ,, ..	50 { 1st 25 c.c. { 2nd 25 c.c.	none none

These figures show that the hydrolytic action of water alone is not great in the time covered by an estimation.

A further sewage experiment showed that if a sewage was distilled with water until it was ammonia-free, and if a given quantity of ammonium chloride in excess of water was added to the residual liquid and the latter redistilled, all the ammonia added was given off readily. The organic matter of the sewage does not therefore keep back ammonia.

APPENDIX 3.

Volatilisation of Ammonia from very Attenuated Solutions of Ammonium Salts, when these are heated in glass vessels.

It has long been known that, when a strong solution of ammonium chloride is warmed, a considerable quantity of ammonia escapes. But, so far as we are aware, no one has published the fact that all the ammonia escapes with the steam on distilling a very attenuated solution of an ammonium salt from a glass vessel, even if that solution contains a trace of acid. On discussing the point in the beginning of the year 1899 with the late Dr. A. P. Aitken, of Edinburgh, we found that he had already made the same observation, but had never published it. As Sir William Ramsay pointed out, this volatilisation was in direct contradiction to the electrolytic dissociation theory. It did not arise from the salt as a whole being carried over, for no hydrochloric acid (of the ammonium chloride) was found in the distillate. It was some time before it occurred to us that this volatility might be due to the action of the alkali in the glass ; but subsequent similar experiments made with a platinum basin (in default of a platinum still) showed that this was the cause.

It will be noticed that the quantities of ammonia volatilised are quite appreciable when compared with the amounts in a sewage, an effluent, or a water.

The ammonia was added as chloride, sulphate, or nitrite, and the distillates were nesslerized in the usual way.

Distillation in a Glass Retort.

—	NH$_3$ taken (Grms.) :	NH$_3$ found (Grms.) :	—
NH$_3$ (as NH$_4$Cl)	·00004 in 100 c.c. water	·0000395	Practically all came over in the first 50 c.c.
,, ,, ...	·00020 in 100 c.c. water	·00019	,, ,,
,, ,, ...	·00097 in 140 c.c. water	·00094	This required two additions of 75 and 50 c.c. water, and re-distillation.
,, ,, ...	·00664 in 175 c.c. water	·00398	This went on for a very long time, with many additions of water.
,, [as (NH$_4$)$_2$SO$_4$] ..	·00005 in 150 c.c. water	·00005	Came over in the first 50 c.c.
,, (as NH$_4$Cl + 2H$_2$SO$_4$)	·00090 in 150 c.c. water	None ..	———
., (as NH$_4$Cl + ¼H$_2$SO$_4$)	·00101 in 150 c.c. water	Only about 1 percent.of the whole.	In first 50 c.c.
,, (as NH$_4$Cl + $\frac{1}{10}$H$_2$SO$_4$)	·00103 in 150 c.c. water	About 10 per cent.of the whole.	In first 50 c.c.
,, (as NH$_4$Cl + $\frac{1}{10}$H$_2$SO$_4$)	·00101 in 120 c.c. water	·00073	This required four additions of water of 100 c.c. each.

The reaction of this last solution to litmus paper was tried after the distillation. There was no perceptible change in the blue litmus after ten minutes.

Distillation of dilute solutions of Ammonium Salts in a Platinum basin, the residual liquid being nesslerized.

—	NH$_3$ taken (Grms.) :	NH$_3$ found in the residue (Grms.) :
NH$_3$ (as NH$_4$Cl)	·000050 in about 100 c.c. water, which was evaporated down to 50 c.c.	·000050
,, (as NH$_4$Cl)	·000052 in 100 c.c. water, boiled down to 50 c.c.	·000049
,, (as NH$_4$NO$_2$)	·000192 in 160 c.c. water, boiled down to about 50 c.c. and made up to 100 c.c. with distilled water.	·000166

APPENDIX 4.

Influence of Nitrates on the above Kjeldahl Method (p. 26).

With regard to the estimation of *Nitric Nitrogen* by this Kjeldahl method —when the zinc is dissolved rapidly by adding the whole 10 c.c. of sulphuric acid at once, the reduction of nitrate to ammonia is very incomplete ; this is proved by the following two determinations made with a solution of pure potassium nitrate :—

	I.	II.
Nitric Nitrogen taken (grms.)	0·008078	0·005993
Nitrogen found by Kjeldahl (grms.) ..	0·006152	0·004260
Loss	0·001926	0·001733
Percentage loss	23·8	28·9

But when the slow reduction method is followed with solutions of pure potassium nitrate, the error does not exceed about 3 per cent. of the total quantity taken, as is shown by the following three estimations :—

Grms. Nitric Nitrogen taken in 200 c.c. Distilled Water.	Equal to Parts Nitric Nitrogen per 100,000.	Nitrogen found by " Kjeldahl."	Loss.	Percentage Loss.
I. 0·011821	5·91	0·011543	0·000278	2·4
II. 0·011633	5·81	0·011226	0·000407	3·5
III. 0·011633	5·81	0·011190	0·000403	3·5

In order to see whether a closer approximation (than the foregoing error of 3 per cent.) to the estimation of the nitric nitrogen in a solution of pure potassium nitrate could be obtained by using aluminium foil and caustic potash for reduction, instead of zinc and acid, a few experiments were made as follows :—

From 0·5 to 1·0 grm. aluminium foil and 10 c.c. of the purified potash were used for each estimation, which was made in a tightly-corked flask fitted with a valve containing a little dilute sulphuric acid, so as to trap any ammonia that might escape from the alkaline liquid. After reduction the whole was boiled down with strong sulphuric acid in the usual way, no sodium sulphate being however added. The results showed a loss of 6 to 12 per cent. of nitric nitrogen upon quantities of 0·006 grm. nitric nitrogen in 100 c.c. of liquid.

There was also the further objection that the cake of aluminium sulphate did not dissolve in the boiling sulphuric acid during the last stages of heating, and hence it was practically impossible to disintegrate all the carbonaceous (and nitrogenous ?) matter.

The loss per cent. would, of course be smaller in a solution containing nitrogen in the form of ammonium salt as well as of nitrate (assuming that no compound of nitrogen is present which escapes reduction). Thus, with

solutions containing ammonium chloride alone, the Kjeldahl method gave the following results :—

Parts per 100,000.

Ammoniacal Nitrogen taken (presumably in 200 c.c. water).	Nitrogen found by " Kjeldahl."	Gain or Loss.	Percentage Gain or Loss.
I. 4·117	4·121	+ 0·004	+ 0·10
II. 2·061	(a) 2·133 ⎫ Two deter-	+ 0·072 ⎫	+ 3·5
	(b) 2·065 ⎭ minations	+ 0·004 ⎭	+ 0·19
III. 2·061	2·045	− 0·016	− 0·78

Rejecting II (a) as being probably a bad estimation, the other figures found are very near those required by theory.

Influence of Nitrites on the above Kjeldahl Method.

The following mixed solutions (each in 200 c.c. distilled water), which consisted mainly of salts of ammonium together with very considerable quantities of nitrite, but very little nitrate, gave :—

Parts per 100,000.

Nitrogen taken as :			Total Nitrogen taken.	Nitrogen found by " Kjeldahl."	Gain or Loss.	Percentage Gain or Loss.
Ammonium Chloride.	Potassium Nitrite.	Potassium Nitrate.				
2·061	0·038	0·005	2·104	2·181	+ 0·077	+ 3·7
2·061	0·383	0·049	2·493	2·526	+ 0·033	+ 1·3
1·095	0·076	0·004	1·175	1·205	+ 0·030	+ 2·6
1·095	0·152	0·007	1·254	1·225	− 0·029	− 2·3
2·061	0·383	0·049	2·493	2·474	+ 0·019	− 0·8

These results prove that amounts of nitrous nitrogen, such as are usually found in sewage effluents, are estimated—within the limits of experimental error—by this slow-reduction Kjeldahl process. The following figures, however, show that this is not the case with solutions containing large amounts of nitrous nitrogen (3 to 4 parts per 100,000), quantities far in excess

APPENDIX 4—*continued.*

of any that we have ever found in land effluents, or indeed in any sewage effluent with possibly only one exception :—

Parts per 100,000.

Nitrogen taken as :		Total Nitrogen taken.	Nitrogen found by " Kjeldahl."	Loss.	Percentage Loss.
Potassium Nitrite.	Potassium Nitrate.				
3·832	0·488	4·320	3·460	0·860	22·5
2·980	1·830	4·810	3·990	0·820	27·4

This loss is doubtless caused by lower oxides of nitrogen escaping from the acid liquid before the nascent hydrogen has had time to reduce them. It would therefore be advisable, when a Kjeldahl estimation has to be made of a solution containing a great deal of nitrite, to first convert that nitrite into nitrate by means of pure permanganate solution.

APPENDIX 5.

E. Halliwell's Table showing Dissolved Oxygen Absorption by Sewage Liquors and Effluents, (a) in five days at 18·3° C.; (b) in three days at 26·7° C. (at various dates between January, 1924, and January, 1926).

	Parts per 100,000.			
			SAME SAMPLES PLACED IN ORDER OF DISSOLVED OXYGEN TAKEN UP.	
	Dissolved Oxygen taken up in		Dissolved Oxygen taken up in	
Treatment of Sample.	5 days, at 18·3° C.	3 days, at 26·7° C.	5 days, at 18·3° C.	3 days, at 26·7° C.
Septic, sprinklers, and irrigation	2·84	2·86	·16	·12
Septic, sprinklers, filtration and irrigation	·50	·56	·48	·56
Open septic	12·56	11·32	·50	·56
Septic, sprinklers, and sedimentation	1·32	1·32	·50	·60
Septic, sprinklers, sedimentation and irrigation	2·0	1·84	·52	·60
Precipitation and irrigation, No. 2 outlet	2·36	2·20	·77	·70
Precipitation and irrigation, No. 1 outlet	·96	·92	·80	·88
River Chor, to sewer ..	1·60	1·28	·86	·92
Precipitation, sprinklers, and sedimentation	4·5	4·2	·92	1·10
Septic, sprinklers, sedimentation and filtration	1·88	1·84	·96	1·16
(1) Septic, sprinklers and sedimentation ; (2) settlement	7·56	7·24	·96	1·04
Septic, sprinklers, and sedimentation	1·0	·76	·96	·92
Open septic, sprinklers, and sedimentation	1·12	1·14	1·0	·76
Septic, sprinklers, sedimentation and irrigation	2·02	2·04	1·12	1·14
Discharge from sewer ..	35·2	31·3+x	1·12	1·20
Septic, sprinklers, and sedimentation (south)	4·64	4·52	1·24	1·42

APPENDIX 5—*continued*.

E. Halliwell's Table—*continued*.

	Parts per 100,000.			
			SAME SAMPLES PLACED IN ORDER OF DISSOLVED OXYGEN TAKEN UP.	
Treatment of Sample.	Dissolved Oxygen taken up in		Dissolved Oxygen taken up in	
	5 days, at 18·3° C.	3 days, at 26·7° C.	5 days, at 18·3° C.	3 days, at 26·7° C.
Septic, sprinklers, and sedimentation (north)	3·52	3·44	1·24	1·28
Open septic, sprinklers, sedimentation and irrigation	·50	·60	1·24	1·16
Septic, sprinklers or contact beds, and irrigation	·96	1·16	1·32	1·32
(1) Settlement and land ; (2) settlement, land and filtration	1·78	1·80	1·44	1·28
Discharge from flash ..	·52	·60	1·44	1·52
Settlement and irrigation ..	7·12	7·36	1·60	1·28
Precipitation and filtration	2·10	2·20	1·60	1·68
Septic, sprinklers and sedimentation	2·08	1·96	1·60	1·64
Precipitation, filtration, and irrigation	·86	·92	1·65	1·60
Precipitation and filtration..	·48	·56	1·68	1·84
(1) Septic, sprinklers, and irrigation ; (2) septic and irrigation	2·88	3·0	1·78	1·80
Septic, sprinklers, and sedimentation	4·52	4·28	1·84	2·14
Septic, contact, and irrigation	4·8	4·48	1·88	1·84
Irrigation	8·32	7·52+x	1·92	1·88
Discharge from land ..	47+x	42·8+x	2·0	1·84
Septic, sprinklers, and irrigation	·96	1·04	2·02	2·04
Discharge S.W. tanks ..	12·5	12·0	2·08	1·96
Septic, filtration, and irrigation	9·12	8·96	2·10	2·20
Settlement and irrigation ..	1·44	1·28	2·10	2·00
Precipitation and filtration	3·50	3·48	2·12	2·16
Precipitation and irrigation, Wham Ditch ..	2·24	2·64	2·24	2·64
Precipitation and irrigation, No. 2 outlet	6·72	7·04	2·24	2·32

E. Halliwell's Table—*continued*.

Parts per 100,000.

Treatment of Sample.	Dissolved Oxygen taken up in		SAME SAMPLES PLACED IN ORDER OF DISSOLVED OXYTEN TAKEN UP.	
			Dissolved Oxygen taken up in	
	5 days, at 18·3° C.	3 days, at 26·7°C.	5 days, at 18·3° C.	3 days, at 26·7° C.
Open septic, sprinklers, sedimentation, and irrigation or filtration	2·12	2·16	2·36	2·20
Septic	22·2	21·2	2·44	2·44
Septic, sprinklers, sedimentation and irrigation	·92	1·10	2·64	2·34
95 per cent. final ; 5 per cent. tank	1·84	2·14	2·84	2·86
85 per cent. final ; 15 per cent. tank	4·28	4·34	2·88	3·0
75 per cent. final ; 25 per cent. tank	6·4	6·32	2·96	2·80
Septic, sprinklers, and sedimentation (north)	1·60	1·68	2·98	2·90
Septic, sprinklers, and sedimentation (south)	3·16	2·92	3·16	2·92
Precipitation and irrigation	1·60	1·64	3·50	3·48
Settlement in storm tanks	21·6	23·6	3·52	3·44
(1) Septic, sprinklers, and sedimentation ; (2) septic and sedimentation	4·1	3·8	3·68	3·52
Precipitation and irrigation	4·80	4·88	3·92	4·0
Septic and irrigation ..	6·88	6·80	4·10	3·8
Septic	14·0	13·4	4·28	4·34
Septic, sprinklers, and sedimentation (north)	2·44	2·44	4·32	4·64
95 per cent. final ; 5 per cent. tank	2·96	2·80	4·50	4·20
85 per cent. final ; 15 per cent. tank	3·68	3·52	4·52	4·28
75 per cent. final ; 25 per cent. tank	4·32	4·64	4·64	4·52
Precipitation and filtration	·16	·12	4·8	4·48
Septic and sprinklers ..	2·10	2·0	4·8	4·88
Settlement and irrigation ..	1·24	1·16	5·36	4·9
Septic, sprinklers, and sedimentation	1·65	1·60	6·4	6·32

APPENDIX 5—*continued.*

E. Halliwell's Table—*continued.*

Parts per 100,000.

Treatment of Sample.	Dissolved Oxygen taken up in		Same Samples Placed in Order of Dissolved Oxygen taken up.	
			Dissolved Oxygen taken up in	
	5 days, at 18·3° C.	3 days, at 26·7° C.	5 days, at 18·3° C.	3 days, at 26·7° C.
Settlement, irrigation and filtration	·77	·70	6·72	7·04
Precipitation, filtration and irrigation	6·96	6·80	6·76	6·32
Septic, sprinklers or filtration and irrigation	1·24	1·42	6·88	6·80
Septic and (1) filtration and irrigation ; (2) irrigation	2·64	2·34	6·96	6·80
Drainage from sludge beds	66·4	62·4	7·12	7·36
Septic, sprinklers, sedimentation and irrigation	5·36	4·9	7·56	7·24
Septic, sprinklers or filtration and irrigation	1·68	1·84	8·3	7·2
Settlement and irrigation ..	18·2	17·0	8·32	7·52+x
Settlement and irrigation ..	8·3	7·2	9·12	8·96
(1) Precipitation and filtration ; (2) crude irrigation	6·76	6·32	12·50	12·00
Septic, sprinklers and sedimentation (north)	1·44	1·52	12·56	11·32
Septic and double filtration	2·98	2·90	14·0	13·4
Septic, sprinklers and sedimentation (north)	1·24	1·28	18·2	17·0
Septic, sprinklers and sedimentation (south)	3·92	4·0	21·6	23·6
Crude sewage	22·8	21·6	22·2	21·2
Activated sludge æration and settlement	·80	·88	22·8	21·6
Septic, sprinklers, sedimentation and filtration	1·92	1·88	35·2	31·3+x
Septic, sprinklers and sedimentation (south)	2·24	2·32	47·0+x	42·8+x
Septic, sprinklers and sedimentation (north)	1·12	1·2	66·4	62·4

APPENDIX 5—*continued.*

R. Eaton's Table showing Dissolved Oxygen Absorption by Effluents, (a) in five days at 18·3° C.; (b) in three days at 26·7° C. (at various dates between March and June, 1925, inclusive).

Incubated 5 days at 18·3° C.	Incubated 3 days at 26·7° C.
1·74	1·73
1·31	1·28
1·27	1·28
1·98	1·95
1·95	2·10
1·70	1·92
2·40	2·16
4·32	4·16
6·84	6·64
1·29	1·39
7·36	7·36
1·76	1·73
4·0	4·08
1·28	1·22
2·7	2·59
3·88	3·88
1·39	1·34
1·99	2·02
·72	·84
1·68	1·72
2·0	1·92
1·13	1·01
1·48	1·12
3·7	3·4
2·9	2·8
2·7	2·7
3·6	3·28
0·92	1·00
3·20	3·20

APPENDIX 6.

Miller Dissolved Oxygen Test (using Paraffin Oil).

Comparison of Determinations with results given by the Winkler Method (Ardern).

Character of Sample.	Dissolved Oxygen : parts per 100,000.	
	Winkler.	Miller.
Activated sludge effluent	0·70	0·80
,, ,, ,, ...	0·37	0·47
,, ,, ,, ...	0·86	0·83
,, ,, ,, (diluted)	0·91	0·83
Primary contact bed effluent	0·46	0·44
,, ,, ,, (1/10 dilution)	0·93	0·84
,, ,, ,, ,, ,,	0·81	0·79
,, ,, ,, ,, ,,	0·74	0·69
,, ,, ,, ,, ,,	0·83	0·80
,, ,, ,, (undiluted) ..	0·23	0·26
Secondary contact bed effluent	0·83	0·86
,, ,, ,, (1/5 dilution)	0·86	0·80
Mean result	0·71	0·70

Dissolved Oxygen Absorption—Royal Commission Test.

| —	Winkler.	Miller.
	2·21	2·00
	2·21	2·21
	2·61	2·69
	2·03	2·21
	2·56	2·81
	2·59	2·61
	1·50	1·47
Various samples of Effluent from the Activated Sludge process	1·11	0·94
	1·86	2·28
	2·03	2·21
	2·17	2·29
	1·71	2·08
	1·76	1·74
	1·69	1·54
	1·79	1·54
	1·47	1·44
Mean result	1·96	2·00

APPENDIX 7.

Sludge Analysis.

Alternative Method for Grease Determination.

There are a few sludges with which it is found that repeated washing gives results as accurate as the Soxhlet method, a great saving of time thus resulting. Where preliminary experiment proves that such is likely to be the case, the dried sludge may be ground in a mortar with 4 or 5 times its volume of Calais sand, thrown on to a filter paper in a funnel and thoroughly washed with petroleum ether, the after procedure being the same as in the Soxhlet method. This method may be used for routine purposes, but for official or comparative purposes the Soxhlet method should be followed.

In cases where the grease is to be determined, it is essential to acidify the sludge with Hydrochloric Acid before drying, in order to decompose any fatty acid salts.

Formerly .

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By
Sir George Newman
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Ministry of Health.

The economic aspect of ill-health is not always the one that is most obvious yet it is startling by reason of the magnitude of the loss involved. It is computed that among insured persons alone, at least 23¼ million weeks' work is lost to the country in the year. Some £13,000,000 is expended annually in Sickness and Disablement benefit. This is but one illustration of our national need to prevent ill-health and incapacity while we may. Sir George Newman's "OUTLINE OF THE PRACTICE OF PREVENTIVE MEDICINE" covers the whole field of prevention in its various branches, and should prove invaluable not only to the medical profession but to the layman desirous of viewing his problem as a whole and avoiding the fallacies of spasmodic "health-stunts." First issued in 1919, this work has been in great demand both at home and abroad, and, while its form remains unchanged, a considerable amount of new matter has been added and the whole has been revised.

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